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## The Plasma Physics of Processing Discharges

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*Plasma Physics Division*

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# THE PLASMA PHYSICS OF PROCESSING DISCHARGES

## 1. Introduction

Plasma processing has grown into a tremendously important industrial capability over the last 20 years, and has done so with virtually no input from traditional plasma physicists. NRL itself is a large user of plasma processing in such areas as nanocircuit fabrication (Code 6804), diamond thin film deposition (Code 6174), superconducting film deposition Code (Code 6340), and nanocube production and deposition (Code 6371). Undoubtedly there are other users in the laboratory also. For the past few years, more traditional plasma physicists have been beginning to see the light and have been attempting to impact this field. There are plasma modeling efforts going on in the major industrial users, and university plasma physicists are beginning to set up programs in the area also. The Plasma Physics Division at NRL is also attempting to become active in this area.

The obvious question is whether plasma physicists are necessary at this late date. Increasingly, a consensus is emerging that the answer is yes. Both the National Research Council<sup>1</sup> and Naval Studies Board<sup>2</sup> have recommended that plasma processing be put on a firmer scientific footing, and point to several areas where industrial processes are limited by the plasma itself. Shohet<sup>3</sup> points out that the markets and potential markets for materials produced by plasma processing is in the hundreds of billions of dollars. Also he quotes several industrial users as needing a better understanding of the plasmas in their devices. The research support in this area in for instance Japan is hundreds of millions of dollars per year, mostly in the industrial sector, but with tens of millions per year in the university sector. This report is based on the assumption that the scientific basis of plasma processing is important both commercially and within the Navy.

Another, although less compelling reason for interest in the area regards its recent history. Flamm and Herb<sup>4</sup> point out that the number of components on an integrated circuit chip has doubled every year from 1960 to 1980. From 1980 to the present, the rate of increase has slowed somewhat, but is still impressive. They point out that this record of rapid innovation, over such a long time, is unmatched in all of world history. Much of this innovation resulted directly from plasma processing, and this alone makes the field interesting in its own right.

This memo attempts to set out in fairly simple form as much of the basic theory of processing discharges as is possible given constraints of reasonable length and simplicity. One thing about plasma processing is that it is very much an interdisciplinary area involving (at least) plasma physics, surface physics, atomic and molecular physics, and chemistry. Reference (3) points out that no single person is knowledgeable in all areas of plasma processing, and this author certainly makes no claim to be the first one. This memo involves mainly the plasma physics; it touches on the atomic physics and chemistry for fairly simple plasmas, and it regards surfaces as passive objects that absorb whatever is incident and (mostly) do not emit anything. Better plasma processing models must ultimately treat the surface as an active substance which itself affects the plasma.

There are a large number of textbooks in plasma physics, and the ones denoted here<sup>5-12</sup> were particularly useful preparing this memo. Furthermore there are several other books devoted to plasma processing<sup>13-15</sup>, and a very extensive one is in preparation<sup>16</sup>. However, amazingly, this author has found virtually nothing of reasonable length, simplicity, and scientific rigor that summarizes the plasma physics of processing discharges. If anything, there may even be a prejudice that chemistry and surface science are what is necessary and the plasma physics is just a witches brew that can never be understood and probably is not very important anyway. Actually, the plasma physics; namely the kinetic theory of charged particle gases and the electro-dynamics of charged and conducting fluids; is a very important part of the problem, and one which can be understood at least in part. In fact there are now many attempts at modeling the plasma both with fluid simulations<sup>17-23</sup>, Monte Carlo modeling of particle streams in sheath fields<sup>24-26</sup>, and full particle simulations<sup>27-34</sup>. There is less analytic work, but nevertheless, analytic work is doable and important<sup>35-38</sup>.

To see the importance of analytic work, consider some of the constraints on fluid and particle simulations. For instance one very interesting fluid simulation is that of Graves and Jensen<sup>18</sup>, which models a simple one dimensional fluid of electrons and ions in a dc or rf discharge. To get a single steady state solution (or in the rf case, a solution periodic with the rf frequency) takes about ten hours of computing on a Cray 1, with what is admittedly a very unoptimized code. However even in the case of Ref.(18), there are eight dimensionless parameters. To scan this sort of space, where

each point is such an involved calculation, is probably out of the question, even with an optimized code and a supercomputer on the head of a pin (manufactured with plasma processing!).

Particle simulations face probably more such difficulties. First of all, the particle simulation has many disparate time scales. The shortest is probably the inverse electron plasma period, and a simulation typically needs about 5 time steps per  $\omega_{pe}^{-1}$ . Thus the time step is about  $10^{-11}$  seconds for a plasma with electron density  $10^{11}\text{cm}^{-3}$ . On the other hand the ion neutral collision time for a room temperature ion in a 0.1 Torr plasma is about  $10^{-5}$  seconds. Hence just to simulate a single ion collision could take as many a million time steps. In practice, either time scales have to be artificially compressed, or else different physical processes have to be approximated. Another difficulty with simulations is that they are inherently dynamic, that is a set of particles starts out at time  $t=0$  and then evolves. As just pointed out, the time scales of the simulations are microseconds, or perhaps as little as hundreds of picoseconds. However processing plasmas are steady state, or are adiabatically evolving if they are affected by the plasma-workpiece interaction. The industrial process is typically on for minutes or hours. Thus to be useful, a simulation must evolve toward a steady state, which it might or might not do, depending on the circumstances.

The point of this is not to disparage particle or fluid simulation, which clearly must play a crucial role in the modeling of plasma processing. Not only is the actual theory very complicated, requiring extensive computation; but keeping track of dozens or hundreds of reaction channels requires a tremendous amount of bookkeeping which can only be done numerically. However this memo emphatically make the case that there is an important role for analytic theory also. Analytic theory can give not only scaling laws, which can reduce the dimensionality of the parameter space, but can give important understanding of physical principles. This does not appear to exist in compact form in other sources.

For instance collision processes are discussed in literally dozens of texts. However there does not seem to be a single source which puts together the information on collisions and kinetic theory relevant to processing plasmas. This is attempted in Secs.2-5 of this report. Scaling is an important concept in plasmas, and in discharge theory,  $E/p$  (the electric field divided by the neutral

pressure) is often regarded as a scaling parameter. However this is not always the case; the requirements for scaling laws are given in Sec.6. A description of the plasma is greatly simplified if a fluid approximation is valid. However, derivations of fluid equations, including transport, for partially ionized plasmas are not easy to find. This is discussed in Sec.7, which relies heavily on Ref.(5).

Where fluid equations are used to describe processing plasmas, they are usually simplified to the point that their singular nature is swept away. However this singularity is responsible for the sheath transition. The derivation of it, as well as an approximation for the neglect of the singularity, is described in Sec.8. Sheaths themselves are a complicated and important part of processing plasmas. One experimental fact, known for decades, is that the anode and cathode sheaths of a dc glow discharge are very different from one another, the latter being inherently collisional. This author has not found a simple explanation for why this is so. For instance why is the cathode voltage drop so much greater than what is required to electrostatically exclude electrons? An explanation does exist and is given in Sec 9. Thus there are important analytic insights and scaling laws which must complement more detailed numerical simulations.

Now we will very briefly discuss some industrial plasma processes, to see what direction they drive the theory. We will start with integrated circuit fabrication, described more fully in the cited books. Typically the challenge is to etch a precise pattern into a silicon or silicon dioxide substrate. Atop the silicon wafer is a mask which has the pattern in it. One would like to expose the covered wafer to something that the cover is impervious to, but which eats away at the silicon. In the early days of integrated circuit fabrication, the etch was usually done chemically. However as characteristic sizes were reduced over the years, chemical etching became less and less satisfactory. For one thing, chemical etching is typically isotropic, so that the mask is undercut by the etch. As tolerances became tighter, this became unsatisfactory since one line etched into the silicon would run into its neighbor. The solution for these narrower line widths, has been to use a plasma etch. The plasma has two advantages, first it produces the etch material in a dry environment, and secondly, the etch is anisotropic, so the trench edge is nearly vertical. To etch silicon, one would like to produce an etch material that reacts chemically with silicon to produce a volatile substance which can be pumped

away. Typically this is  $\text{SF}_4$ , which is gaseous. In wet etching, usually a very corrosive material like HF is used to produce this. One great advantage of the plasma, is that electron collisions produce not only charged particles, but also free radicals like atomic fluorine. When they strike the workpiece however, they react very strongly. These free radicals, which do not exist long in liquids or high density gases, can be readily produced and maintained in the plasma environment because the electrons of the plasma have more than enough energy to generate them. However the electrons, while energetic compared to the background, have such low density that they do not appreciably increase the energy content of the entire gas. Thus a plasma gives rise to the possibility of high energy density chemistry at low gas energy density.

Now let us consider the anisotropic nature of the etch. The workpiece is exposed not only to the neutral free radicals, but also to the streaming ions which form the plasma sheath. The nature of this sheath is controlled mostly by the bulk plasma and the external circuit. If the sheath is reasonably collisionless, the ions and fast neutrals impinge perpendicular to the workpiece. Thus the bottom of the trench will be struck by the ion flux, and the side walls will not be. Thus one possible description of the etch process is that the free radicals react with the silicon to produce a polymer which adheres to the silicon walls and protects the silicon against the etch. However on the bottom, the delicate polymer cannot stand up to the stream of ions and fast neutrals, so the etch occurs and the volatile product is formed and pumped away.

The plasma etch has worked well for separations of above a micron. However with the thrust to quarter and half micron feature separation, existing plasma etch technology is not expected to work as well, and no other scheme other than a more advanced plasma process seems to be on the horizon. While the total process just described involves complicated aspects of surface and gas phase chemistry, the plasma is important also. Specifically we would like a plasma theory to be able to predict the production of free radicals as well as the flux and energy spectrum of fast ions and neutrals to the surface. At low density, the gas chemistry depends mostly on the electron distribution function; and in the cases where a fluid model for the electrons apply, on their density and temperature. The flux and spectrum of fast ions and neutrals to the workpiece depends crucially on how the plasma sheath is set up. These then are the sorts of answers we want from plasma theory, and the sorts of

scalings and physical principles we want from analytic plasma theory.

Another area for which plasma processing has turned out to be very important is the deposition of thin diamond films<sup>39-43</sup>. Diamond has remarkable properties regarding hardness, as well as thermal and electrical properties. Until recently, they were available only through natural mining, or high temperature, high pressure compression of carbon. In the last ten years it has been discovered that diamond films could be deposited on substrates by plasma chemical vapor deposition as well as other low pressure means. This then is the opposite of the plasma etching, here the plasma is needed to add an additional layer to a substrate.

The actual deposition process is very complicated and does not seem to be well understood at this point. If a layer of carbon is deposited on a substrate, the energetically favored form is graphite, not diamond. However since the particle stream impinging on the substrate is quite energetic, there is sufficient energy flux to form the less favorable diamond structure. Typically, a large fraction of the deposited carbon is in graphite form, and a much smaller part of the deposited carbon is in the diamond structure. The idea then is to eat away the graphite as rapidly as it builds up, so that what is left is a diamond film. This is done in two ways, first by heating up the substrate to keep it less hospitable to graphite and more to diamond, and second to have a flux of free radicals on the substrate. The flux of free radicals also eats away at the graphite. It seems certain that the flux of free radicals is sufficient, since diamond deposition is observed in plasmaless systems such as acetylene torch deposition systems. However the diamond deposition might be enhanced with an ion flux as well, and furthermore free electrons in the plasma can be a source of free radicals as well as ions.

The original plasma deposition experiments were done with combinations of  $\text{CH}_4$  and  $\text{H}_2$  as the fill gases. Typically the maximum diamond deposition rate is about  $1\mu\text{m}$  per hour, which maximized when the  $\text{CH}_4$  mole fraction is about 2%. For much higher  $\text{CH}_4$  concentration, diamond films do not form. Possible free radicals that can form include  $\text{H}$ ,  $\text{CH}_3$  as well as other hydrocarbon radicals. Since the  $\text{CH}_4$  is the only source of the diamond, it is apparent that much more free radical than pure carbon is required. More recently<sup>43</sup>, diamond films were deposited for fill gases of  $\text{CH}_4$  and  $\text{O}_2$ . Here possible additional free radicals include  $\text{O}$  and other oxygen

compounds. For this  $\text{CH}_4\text{-O}_2$  plasmas, it was found that diamond deposition was both faster and the quality of the diamond film was higher. Deposition rates in excess of  $5\mu\text{m}$  per hour were observed.

For the case of diamond deposition, the plasma seems to play the role of a source of free radicals. These free radicals can only come from electron interactions with the background gases. Thus what one needs from a theoretical model is the electron density and temperature (or electron distribution function if the electrons are not Maxwellian) and the free radical production. The electron density and temperature are derived from the basic plasma physics and the coupling of the plasma to the external circuit. The times necessary for reasonable film deposition (hours), also emphasizes the necessity for steady state plasma theory

Finally we will consider the case of Plasma immersed ion implantation (PIII)<sup>3,44</sup>. Often one has a metal, a tool for instance, and one desires to implant guest ions up to a certain depth in the metal, for surface modification. For instance nitrogen is often implanted in steel to harden the surface, and/or to reduce the surface friction. To implant the nitrogen to the necessary depth, it must be driven into the metal at energies of typically 100 keV and higher. At first one might think an ion accelerator would be required. However this has disadvantages in that the ions all are accelerated in one direction and the workpiece might not be planar. An alternative would be to put the workpiece in a plasma and pulse it with a negative voltage pulse. Then ions will be accelerated from the plasma into the workpiece. As long as the object is large compared to the plasma sheath, the ions will be accelerated perpendicular to the surface. We would like a plasma theory to tell us the ion dose in terms of the plasma and external circuit parameters.

The theory we work out in this report is guided by what appear to be the needs for the plasma processors just described. One of the most intimidating things about processing discharges is that they are not only collisional, but there are an enormous number of different species, collisional and reactive processes. For instance Plumb and Ryan<sup>45</sup>, used 49 reactions to model the gas phase chemistry of a  $\text{CF}_4/\text{O}_2$  discharge. The next four sections review collision and reaction processes in processing discharges. The description of the microscopic collisional and reaction processes are themselves complicated quantum mechanical calculations which

we will not get into here at all. We will assume that cross sections for the appropriate processes are known and the theory we work out will be in terms of these cross sections. Section 2 reviews the basic physics of simple collisions. The next problem is the kinetic theory of a gas of particles with no internal structure, but which interact with each other via binary collisions. This is described in section 3. There, there are relations between each collision process and its inverse which have important implications for the equilibrium theory. For the case of collisions of particles with no internal structure, these relations are not difficult to see from the basic collisional descriptions. The case of particles with internal structure are described first for the case of atoms in Section 4. As the particles have more and more complicated internal structure, relations between the collision and its inverse become less and less obvious. However these relations are still necessary in order for equilibrium statistics to hold. An alternative is to postulate equilibrium statistics (the validity of statistical mechanics really), so that the relation between the collision and its inverse is imposed in that way.

Section 5 discusses a molecular plasma. This gets even more complicated because now there is chemistry as well as excitations and ionizations. We consider a fairly simple molecular plasma, but one still of importance in processing discharges, the oxygen plasma. The free radical is now atomic oxygen. This can be produced for instance by electron collisional dissociation of oxygen molecules. There appear to be two tractable limits, the low density limit where the chemistry is dominated by electron two body reactions, and the very high density limit where the plasma is nearly in thermal equilibrium. For intermediate densities, where 2, 3, 4 or many particle interactions are important, appears to be very complicated. For the most part we consider the low density limit. For this plasma, there are still a large number of possible components. Even neglecting atomic and molecular excited states, which are often important, there are still six components,  $O_2$ ,  $O$ ,  $O_2^+$ ,  $O^+$ ,  $O_2^-$ , and electrons. The number possible of reaction channels is huge. Limiting the reaction rate to below a particular value, we find nine possible reactions, so that there can be different reaction chains which start and end at the same place. For thermal equilibrium to hold, there must be relations between these seemingly independent reaction rates. For the homogeneous plasma with rate equations specified, one thing that is not difficult to see, is that low density equilibrium atomic and ionic distributions reasonably like those

measured, are not possible. Thus the distributions are determined by more than the chemistry. As we will see, the plasma physics must play a crucial role also.

The full processing plasma is described by the Vlasov equation for all species coupled to Maxwell's equations for the fields. These are much too complicated to solve, or even simulate. However for plasmas dominated by binary collisions, there are scaling laws, which in some cases can relate solutions to one another. This is described in Section 6.

Solving the Vlasov equation involves following the time dependence a function of 6 variables, three velocity dimensions and three position dimensions. A fluid formulation however has only three spatial dimensions, so if there is any justification for it, it is greatly simpler than a Vlasov formulation. The fluid formulation for the charged species in the presence of the neutrals is derived in Section 7. Wherever possible, we use a fluid formulation in the cases treated here.

Typically most of the plasma volume is quasi-neutral and there is not large charge separation between the electrons and ions. Thus it is very convenient to make an assumption of quasi-neutrality in the bulk plasma, and this simplifies the fluid description further. However near walls, the quasi-neutrality approximation breaks down and charge separation becomes important. This breakdown manifests itself in the steady state quasi-neutral solution by the presence of a singularity<sup>46-48</sup>. This singularity signals that the quasi-neutral central part must transition into a non-neutral sheath. This can be a very complicated mathematical problem, although in the cases discussed here, it turns out to be not too difficult. Typically the sheath width is very small compared to the other lengths in the plasma, including the mean free path. Thus a fluid model is not necessarily valid for the sheath. However there are often other simplifications, for instance the neglect of collisions or a one dimensional structure. This is discussed in Section 8.

Finally Sections 9 and 10 discuss specific plasma configurations, the dc and rf discharge. They show how the quasi-neutral part couples to the sheath and how mass, momentum and energy are coupled from the external circuit to the plasma. Typically energy is coupled into the bulk of the plasma from the

circuit, although there are mechanisms to couple in through the sheath also for rf plasmas. Energy that is not radiated away or lost to neutrals is convected out through the sheath. Thus the sheath physics must be known in order to calculate the energy balance.

## 2. Particle Collisions in Processing Discharges

Since processing discharges are weakly ionized, the most important collision processes are those with the background neutral gas (and also of course with the walls of the discharge). Here we briefly review the basic binary collision processes. Many different types of elastic and inelastic collision processes are important at one time or another, particularly, and we will generally describe these as they become necessary. First we consider binary collisions between two particles labeled with subscript a and b. The initial velocities are  $\mathbf{v}_a$  and  $\mathbf{v}_b$ , and the masses are  $m_a$  and  $m_b$ . The center of mass velocity is given by

$$\mathbf{v}_0 = (m_a \mathbf{v}_a + m_b \mathbf{v}_b) / (m_a + m_b) \quad (2.1)$$

and the relative velocity is given by

$$\mathbf{v} = \mathbf{v}_a - \mathbf{v}_b \quad (2.2)$$

Velocities after the collision are denoted by primes. If the energy change in the collision is denoted by  $\Delta E$ , corresponding to a change of an internal state of one of the colliding particles, conservation of momentum and energy gives the result

$$\mathbf{v}_0 = \mathbf{v}_0', \quad \mu v^2/2 = \mu v'^2/2 + \Delta E. \quad (2.3)$$

where  $\mu$  is the reduced mass  $m_a m_b / (m_a + m_b)$ . For the case of light particles colliding with heavy particles, as is the case for electron atom collisions in a processing discharge, the reduced mass is very nearly the electron mass. For an atom and an ion of the same species, it is half the mass. Thus, according to Eq.(2.3), the change of internal energy can come only from the motion about the center of mass. If the two input velocities  $\mathbf{v}_a$  and  $\mathbf{v}_b$  are known, conservation of momentum and conservation of energy (assuming  $\Delta E$  is specified) give four of the six unknown velocity components for the particles after the collision. We define the other two components in terms of two collision angles. In the center of mass frame, each particle is scattering from the fixed center of mass. Each particle then scatters through an angle  $\theta$  in this frame. The orientation of the scattering plane with some fixed plane defines another angle  $\phi$ . These two angles then completely define the scattering problem.

Look now at the orbit of particle a with respect the center of mass position. The initial orbits are antiparallel lines displaced from each other, and the center of mass position is somewhere between these lines. These line define a plane. As long as the force between the particles is a central force, the particles, as they scatter from one another never leave this plane. The minimum distance of the linear orbit of for instance particle a from the center of mass position defines an impact parameter b. The particular interparticle potential then determines the scattering angle  $\theta$  in terms of b. Of course this scattering angle is a function of center of mass velocity v. The relation between b and  $\theta$  defines the scattering cross section as

$$\sigma(\theta, v) \sin\theta d\theta = b db \quad (2.4)$$

Here  $\sigma(\theta, v)$  relates the flux of exiting particles scattered into a unit solid angle to the flux of input particles incident at a particular impact parameter. Almost always published graphs of scattering cross section are integrated over angle, so that what is shown is perhaps  $\int \sigma(\theta, v) d\Omega$ , for estimates of total number of collisions, or  $\int \sigma(\theta, v)(1-\cos\theta) d\Omega$ , for estimates of momentum or energy change. Here  $\Omega$  denotes solid angle.

In an elastic collision ( $\Delta E=0$ ), Eq.(2.3) shows that the magnitude of the relative velocity of the two particles remains the same before and after the collision. Thus the relative velocity simply rotates through the angle  $\theta$  in the scattering process. One can easily calculate that the change in momentum of particle a is

$$\Delta \mathbf{p}_a = -\mu(1-\cos\theta)(\mathbf{v}_a - \mathbf{v}_b) \quad (2.5)$$

A straightforward calculation of the energy change of particle a gives the result

$$\Delta K_a = -k(1-\cos\theta)[2K_a - 2K_b + (m_b - m_a)\mathbf{v}_a \cdot \mathbf{v}_b] \quad (2.6)$$

where

$$k = [\mu/(m_a + m_b)]$$

Notice that if the masses of the particles are very different, as with the case of electrons (b) and atoms (a) in a processing discharge, the change of momentum can be comparable to the incident momentum whereas the change in energy is reduced by roughly a factor of  $2m_b/m_a$ . Thus in a plasma, temperature equilibration is generally a much slower process than say momentum exchange. This is the reason that processing discharges can be nearly in equilibrium even though the gas and ion temperature is much less than the electron temperature. The ion and gas temperatures are nearly equal however.

Let us now calculate the force between electrons and atoms in a discharge if they have an average drift with respect to one another. This is

$$\mathbf{F}_e = -\mu \int d^3v_e d^3v_a n_e n_a f_e f_a (\mathbf{v}_e - \mathbf{v}_a) v \sigma_p(v) \quad (2.7)$$

where

$$\sigma_p(v) = \int d\Omega \sigma(\theta, v) (1 - \cos\theta) \quad (2.8)$$

where  $n_e$  is the electron number density,  $f_e$  is the electron distribution function normalized to unity over velocity, and analogously for atoms. Since momentum is conserved, there is an equal and opposite force on the atoms. To evaluate the integrals, one would have to calculate the magnitude of the relative velocity in terms of  $\mathbf{v}_e$  and  $\mathbf{v}_a$ . We do this in Section 6 where fluid equations are derived, and assuming a fairly simple collision model. A similar calculation for the kinetic energy exchange between isotropic distributions electron and atoms (corresponding to temperature equilibration) is given by

$$K_e' = -k \int d^3v_e d^3v_a [2K_a - 2K_e + (m_e - m_a) \mathbf{v}_a \cdot \mathbf{v}_b] n_e n_a v \sigma(v) \quad (2.9)$$

with an equal and opposite term for the atoms. We evaluate this also in Section 6.

Of course there are many other processes going on besides elastic collisions. For instance there is dissociation of molecules, excitation of all species, production of metastables, ionization etc. Since the electrons are the energetic species in processing discharges, electron collisions are the source of virtually all such

processes of interest. An important exception is the generation of fast neutrals. Since electron collisions cannot energize heavy particles, these are produced by ions accelerated in the sheath regions followed by charge exchange collisions. The study of such collision processes is a large subject. For the purpose of the plasma physics of such discharges, we take as given the cross sections of the processes involved, and discuss other separate processes where they become necessary. Important cross sections are tabulated in many places. Usually the cross sections are given as integrals over angle, so they are given as functions of energy alone.

Once the cross sections are given, the rate for the process can be calculated. For instance let us say the process of interest is the ionization of background atoms by electron impact. The impact ionization cross section is then given as some function of  $v$ . The rate at which ions are produced by impact ionization is then given by

$$n_e' = \int d^3v n_e n_a v \sigma_i(v) f_e \equiv \alpha_i(T_e) n_e n_a \quad (2.10)$$

Since it takes some minimum energy to impact ionize an atom, the electron temperature must be sufficiently high, or else there will be very little ionization. However the temperature can be less than the ionization energy, because higher energy electrons in the electron distribution function can still provide significant ionization. Let us anticipate the result that the electron distribution function is Maxwellian. Then take the relative velocity between the electron and atom to be equal to the electron velocity. The ionization cross section is usually linear above the ionization threshold and falls off as roughly  $E^{-1}$  at high energy. An approximate formula for ionization cross section as a function of energy is

$$\sigma_i = 16\sigma_0 E_i (E - E_i) / E(E + 8E_i) \quad (2.11)$$

which maximizes at a value of  $\sigma_0$  at  $E = 4E_i$ . Then for temperatures low compared to the ionization energy, the expression for  $\alpha(T_e)$  can be written as approximately

$$\alpha_i(T_e) = [16\sigma_0/9][8T_e/\pi m]^{1/2} \exp(-E_i/T_e), \quad E_i/T_e \ll 1 \quad (2.12)$$

In an atomic plasma, inelastic collisions consist of electronic excitations as well as ionization and ionization. An analogous calculation can be performed for the excitation rate, and for

temperatures low compared to the excitation energy, one arrives at an expression like Eq.(2.12). Usually these excitations are considered as separate states and the excitation rate for the particular states are calculated as above. Molecules on the other hand have both rotational states (excitation energy of typically  $10^{-4}$ - $10^{-2}$  ev) and vibrational states (excitation energy of typically  $10^{-2}$ -1 ev). While these might be considered separately like electronic excitations, it is generally simpler to consider them as an additional energy drain on the electrons, expressed in terms of an effective  $k$  which at certain electron energies may be much larger than the  $k$  for electron ion collisional energy exchange. For instance for  $N_2$  at about 1 ev,  $k$  can be as large as  $10^{-1}$ . Thus the excitation of molecular vibrations can be an appreciable drain on the electron thermal energy.

### 3. Kinetic Theory for Particles with No Internal Structure

Let us assume that the processing discharge we are considering has mostly atoms, but also electrons and ions. To simplify further, the particles are assumed to have no internal structure, so they are point particles interacting with external fields and also with each other through binary collisions. Since the particles have no internal structure, conservation of energy and angular momentum decree that the collisions are elastic and the internuclear force is a central force. Thus that the interaction is described by an internuclear potential which depends only on particle separation. The distribution function for each particle species is determined by the Vlasov Equation for that species

$$\partial f_a / \partial t + \mathbf{v} \cdot \nabla f_a + (e_a / m_a) [\mathbf{E} + \mathbf{v} \times \mathbf{B} / c] \cdot \nabla_{\mathbf{v}} f_a = C_{aa} + C_{ab} + \dots \quad (3.1)$$

Where the C's on the right hand side denote the contributions to the change in  $f_a$  due to the binary collisions specified. Also, in Eq.(3.1) above, the distribution function  $f_a$  is normalized to local number density rather than unity. Generally with no collision term, Eq.(3.1) is referred to as the Vlasov Equation; with the collision term, the Boltzmann equation. We will use the terms interchangeably here.

We concentrate primarily on the collision terms. When particle b collides elastically with particle a, particles with velocity  $\mathbf{v}_b$  are lost from the distribution function  $f_b$ . As calculated in the previous section, the rate at which particles are lost in a phase space volume  $d^3v d^3x$  is

$$\partial f_b / \partial t (\text{out}) = - \int d^3v_a d\Omega \sigma(\theta, v) v f_a f_b \quad (3.2)$$

In Eq.(3.2) above the integral over  $v_a$  is an integral over all the particles that the particle in question might collide with; here the a subscript might mean a particle of another species, but it also might mean a particle of the same species that collides with particle b and knocks it out of its velocity cell  $d^3v$ . Note that it is not necessarily obvious from Eq.(3.2) that momentum, energy, or even particle number is conserved. We only know that they are, by our assertion that only elastic collisions between particles with no internal structure are involved, a fact not at all obvious, or even true from Eq.(3.23.2) alone. In fact Eq.(3.2) could also be used to describe inelastic or ionizing collisions.

To show things like conservation of momentum and the like, as well as to complete the description of the collision integral, we must also calculate the rate at which particles are scattered into the velocity cell  $d^3v$  centered at  $v_b$ . This is

$$\partial f_b / \partial t d^3v_b(\text{in}) = \int d^3v_b' d^3v_a' \sigma'(\theta', v') v' f_a' f_b' \quad (3.3)$$

where we have denoted with primes the value of the velocities of particles a and b after the collision. The integral over  $d^3v_b' d^3v_a'$  is over only that three dimensional portion of the six dimensional double velocity interval which places the final velocity of particle b within  $d^3v_b$  of  $v_b$ . To proceed, we relate various before and after collision values. First of all, as we saw in the last chapter. The primed parameters are those velocities which give velocities  $v_a$  and  $v_b$  after the collision. As we saw in the last section, the magnitude of the relative velocity does not change before and after the collision, so that  $v=v'$ . Then for  $v_a'$  and  $v_b'$ , we take the final products of the initial a:b collision. At this point it is simplest to proceed by working in the center of mass reference frame. By sketching out the path of the particles in the original collision, and then constructing a collision with the the final velocities as incident velocities and with the same impact parameter, it is not difficult to see that the two collisions are the same except for rotations and reflections of the entire collision. Since the assumed central force is independent of such rotations and reflections, the cross section is the same and so is the magnitude of the scattering angle. Thus  $\sigma'(\theta', v') = \sigma(\theta, v)$ . Finally, let us consider the sizes of the velocity elements  $d^3v_a d^3v_b$ . By expressing the collision parameters in terms of center of mass variables, the center of mass velocity is unchanged in a collision, so  $d^3v_0 = d^3v_0'$ . Since the change in velocity about the center of mass is simply a rotation,  $d^3v = d^3v'$  since rotations preserve volume elements. Thus the expression for the total change of  $f_b$ ,  $\partial f_b / \partial t(\text{in}) - \partial f_b / \partial t(\text{out})$  becomes

$$C_{ba} = -\delta_{ab} \int d^3v_a d\Omega \sigma(\theta, v) v [f_a f_b - f_a' f_b'] \quad (3.4)$$

where  $\delta_{ab}=1$  if  $a \neq b$  and  $\delta_{ab}= 1/2$  if  $a=b$ . It accounts for the fact that if  $a=b$ , each collision is counted twice if the factor of  $1/2$  were not present. In order to simplify the notation, we usually will not specifically include the factor separately unless it is specifically required to avoid confusion. Equation (3.4) is the Boltzmann

collision integral for particles with no internal structure. The prime in the second term in the brackets means particle which collide into velocities  $v_a$  and  $v_b$ .

There are several properties of the Boltzmann collision integral which can be easily easily proved. First of all, if  $f$  is initially positive everywhere, it stays positive. If  $f_b$  is positive and were to go negative, it would first have to be zero at some velocity. However if  $f_b=0$  at this velocity, Eq.(3.4) shows that  $C_{ba}$  is greater than zero, so that  $f_b$  would become positive at subsequent times. It is also not difficult to show that the Boltzmann collision integral conserves mass, momentum and energy in the plasma. If  $Y_b$  denotes a component of momentum, mass or energy of the particle  $b$ , the collisional rate of change of  $Y$  is

$$Y' = -\int d^3v_a d^3v_b Y_b d\Omega \sigma(\theta, v) v [f_a f_b - f_a' f_b'] + b \rightarrow a \quad (3.5)$$

where  $Y'$  is the total change of the quantity summed over both colliding species,  $a$  and  $b$ . If we consider the change within a species, the same logic applies. The integrand is symmetric with respect to changing  $a$  and  $b$  so the  $b \rightarrow a$  term can easily be incorporated into the integral. Now since  $v_a$  and  $v_b$  are simply variables of integration, we can label them as  $v_a'$  and  $v_b'$  in Eq.(3.5). Then, using the fact that for the elastic collision between particles having no internal structure,  $d^3v_a d^3v_b d\Omega \sigma v = d^3v_a' dv_b' d\Omega' \sigma' v'$ , as we have just shown, we find that

$$Y' = -\int d^3v_a d^3v_b d\Omega v \sigma(\theta, v) \{Y_a + Y_b - Y_a' - Y_b'\} [f_a f_b - f_a' f_b'] \quad (3.6)$$

However the term in the bracket  $\{\}$  is simply the sum of the mass, momentum or energy before and after the collision in question. Since mass, momentum and energy are conserved in the collision, this bracket vanishes, thereby proving that mass, momentum and energy are conserved for the entire plasma by the Boltzmann collision integral.

Next we prove the Boltzmann H theorem, essentially a proof that entropy increases until the plasma reaches an equilibrium state. We define the quantity  $H$  as

$$H = -\sum_b \int d^3v_b f_b \ln f_b \quad (3.7)$$

By multiplying the Boltzmann equation by  $\ln f_b$  and integrating over velocity and space, one can get an equation for the total change of  $H$  over the entire plasma. Let us first consider the convective terms. Since  $[\nabla f_b] \ln f_b$  is the gradient of a function of  $f_b$ ,  $Z(f_b)$ , ( $Z(f) = (1/2)f^2 \ln f - (1/4)f^2$ ), the integral over space vanishes as long as the plasma is isolated so that the boundary terms in the spatial integral vanish. If the terms do not vanish, then there is a flux of  $H$  (an entropy flux actually) into the system from the boundary, which we do not consider here. The contribution to  $dH/dt$  from the  $E \cdot \nabla_v f_b$  vanishes for the same reason, except that now there is no possibility of an end point contribution in the velocity integral since  $f \rightarrow 0$  and  $v \rightarrow 0$ . The contribution from the magnetic term is proportional to  $\int d^3 v_b (\mathbf{v} \times \mathbf{B}) \cdot \nabla_v Z(f_b)$  which also integrated to zero over velocity since the velocity gradient of the cross product in front vanishes. Thus a collisionless plasma conserves  $H$  as long as there are no fluxes in from the boundary.

We now consider the collision terms. By the same logic as was used in the derivation of conservation of mass, momentum and energy, we find that

$$dH/dt = 0.25 \sum_{ab} \int d^3 v_a d^3 v_b d\Omega v \sigma(\theta, v) \{ \ln[f_a' f_b' / f_a f_b] [f_a' f_b' - f_a f_b] \} \quad (3.8)$$

Since the  $f$ 's are everywhere positive, the integrand is positive everywhere also. Thus the conclusion is that  $dH/dt$  is always equal to or greater than zero. Note however that an important step in this proof is the summation over species  $a$  and  $b$ . The  $H$  of one component does not necessarily increase, a decrease of  $H_a$  might be balanced by a larger increase of the  $H$  of the interacting component  $H_b$ . However the total  $H$  increases. Correspondingly, the contribution to  $dH/dt$  of a species through its self interaction also increases. Of course  $H$  cannot increase without limit because  $f$  integrates to unity over velocity; where  $f$  is near zero and  $\ln f$  is large,  $f \ln f$  is of course still small since  $\ln f$  diverges to minus infinity very slowly as  $f$  approaches zero. The one case where  $f$  can be very large is if  $f$  is nearly a delta function in velocity. If  $\delta$  denotes the volume of velocity space for which  $f \neq 0$ ,  $H$  is roughly equal to  $-\ln \delta$ . However here  $H$  goes to minus infinity, not infinity. This is the least likely state for the plasma according to the  $H$  theorem. Since  $H$  increases or else vanishes, and it is bounded from above, the plasma must evolve toward a state in which  $H' = 0$ .

Hence the H theorem allows one to derive an equilibrium distribution function for the plasma. We begin by considering the case of a homogeneous plasma with no external forces. Clearly  $\partial f/\partial t$  will vanish as long as

$$f_a f_b - f_a' f_b' = 0 \quad (3.9)$$

or as long as

$$\ln f_a + \ln f_b = \ln f_a' + \ln f_b' \quad (3.10)$$

Recall that  $a$  and  $b$  denote particle parameters before a binary collision, and  $a'$  and  $b'$  denote the values after the collision. Thus the natural log of  $f$  must be one of the quantities conserved in the collision. There are three and only three such quantities so conserved, the mass, momentum and energy. Thus the equilibrium distribution function must be

$$f_b(v) = n_b (m_b/2\pi T)^{3/2} \exp[-(m_b/2T)|v-u|^2] \equiv n_b f_{mb} \quad (3.11)$$

Notice that  $T$  (the temperature or  $2/3$  of the thermal energy) and  $u$  (the average velocity) have no subscript. These values must be the same for the each species of the plasma if it is to be in thermal equilibrium. The constants in the distribution function are chosen so that when integrating over the velocity, the result is the density  $n_b$ . The thermal energy of the species  $W_b$  is obtained by integrating  $1/2 m_b |v-u|^2$  over the distribution function, giving  $W_b = 3n_b T/2$ .

To conclude, we consider the equilibrium distribution function for a non flowing species of plasma in an external force. For convenience, we will take the case of charged particles in an electrostatic potential. As we have seen, a local Maxwellian distribution function is a thermal equilibrium distribution function as long as interparticle collisions are the only thing taken into account. We then consider what spatial dependence will render the Maxwellian distribution an equilibrium distribution in the external field. That is we consider a distribution function of the form

$$f_b = n_b(r) f_{mb} \quad (3.12)$$

Because the velocity distribution is considered to be Maxwellian (with the same temperature for all species), the collision term in

the Boltzmann equation vanishes. Thus if a density can be determined so that

$$\mathbf{v} \cdot \nabla n_b f_{mb} - n_b (e_b/m_b) \nabla \Phi \cdot \nabla_{\mathbf{v}} f_{mb} = 0 \quad (3.13)$$

the equilibrium distribution in the external force can be obtained. One can easily show by direct substitution that an  $n_b$  can be found and is

$$n_b = n_{b0} \exp -e_b \Phi / T \quad (3.14)$$

where  $n_{b0}$  is the number density of species  $b$  at  $\Phi=0$ . For a single species, getting the distribution in an externally provided electrostatic potential is not difficult as we have just shown. For a plasma which comprises several species of very different masses and positive and negative charges, the thermal equilibrium distribution function in the external field can be considerably more complex if it exists at all. If the electrostatic field is itself generated by the charge separation in the plasma, and the charged species in the plasma are ions and electrons, we must have

$$\nabla^2 \Phi = 4\pi e (n_e - n_i) \quad (3.15)$$

as well as Eq.(3.14) for thermal equilibrium. Notice that in a falling potential, the electron density decreases while the ion density increases. The decrease of electron density with decreasing potential results from thermal electrons being reflected from the potential, so there are fewer electrons at low potential than at high potential. There are certain cases in a plasma where this is a valid description of the equilibrium; however more often it is not, particularly for the ions. In ion sheaths, the ions typically stream into the falling potential of the sheath from the bulk plasma. The ions, in contrast to the electrons accelerate as a fluid. Hence, as the ions speed up in the sheath, their density drops. As we will see, the fact that the electrons and ions have very different masses and opposite charges usually means that if there are electric fields present, at least one species is out of equilibrium.

#### 4. Kinetic Theory and Rate Equations for Atoms

In this section, we extend the kinetic theory calculations to the cases where the particles do have internal structure. We consider the case of atoms since their internal structure is the simplest, there being no rotational or vibrational states of the particle. However there are atomic excitations and as well as ionization. We first consider the case of excitations alone. In the binary collision, particle a has excitation energies  $E(a,j)$ , where the index  $j$  denotes the various atomic excitations. The distribution function now has an additional index  $j$  to account for the excitation state of the particle.

To derive the kinetic equation for the case where the particle's have internal degrees of freedom, we follow the procedure of the previous section. Specifically, Eq.(3.2) still applies and the rate of particles of species  $b$  and internal energy  $E(b,j)$  scattered out of the region of velocity space is

$$\partial f_{bj}/\partial t(\text{out}) = -\sum_i \int d^3v_a d\Omega \sigma(\theta, v, E(b,j), E(a,i)) v f_a f_b \quad (4.1)$$

The particles scattered in are given by

$$\partial f_{bj}/\partial t(\text{in}) d^3v_b = \sum_{i'j'} \int d^3v_a d^3v_b' \sigma'(\theta', v', E(b',j'), E(a',i')) v' f_{a'} f_{b'} \quad (4.2)$$

The integral over velocity variables and summation over  $i'j'$  in Eq.(4.2) is only over those primed velocities which put the final collision products within  $d^3v_a d^3v_b$  of  $v_a$  and  $v_b$  after the collision; and over those  $i'j'$  which leave the particle  $b$  in energy  $E(b,j)$  and particle  $a$  in energy  $E(a,i)$ .

For the case of elastic collisions of particles with no internal structure, the relation between velocity interval, relative velocities and cross sections for the forward and reversed collision provided crucial information which simplified the collision integral and verified Boltzmann statistics. This no longer holds true for the individual factors in the integral for the case where the atoms have internal structure. For instance  $v$  (recall it is the magnitude of the relative velocity in the center of mass frame) is no longer constant in an inelastic collision, which implies also that  $d^3v = [v^3/v'^3] d^3v'$ . Thus the individual equalities no longer hold true for the inelastic collisions. However there is a principle, called the principle of

detailed balance which says that the rate if forward and reverse collisions are equal if the populations of the states are equal. This then dictates that the product of the magnitude of the relative velocity times cross section times velocity interval is the same for the forward and reverse process. This is discussed in tests on Statistical Mechanics. It is a subtle point and is required for Boltzmann statistics in equilibrium. Using the principle of detailed balance to relate the rates of the forward and reverse processes, we find that the collisional contribution to  $\partial f_b/\partial t$  is

$$\partial f_{bj}/\partial t = -\sum_i \int d^3v_a d\Omega \sigma(\theta, v, E(b,j), E(a,i)) v [f_{ai} f_{bj} - f_{ai}' f_{bj}'] \quad (4.3)$$

As before, the collisional rate of change of  $f_{bj}$  vanishes if  $f_{ai} f_{bj} - f_{ai}' f_{bj}' = 0$ , or if  $\ln f_{ai} + \ln f_{bj} = \ln f_{ai}' + \ln f_{bj}'$ . Thus, as before, in equilibrium, the logarithm of the distribution function is proportional to quantities conserved in the collision. These are now the momentum and total energy of the particles, the total energy now being the sum of the internal energy and the kinetic energy. Thus the equilibrium distribution function is now given by

$$f_{b,j} = Q(T)^{-1} \exp[-E(b,j)/T] f_b(v) \quad (4.4)$$

where  $f_b(v)$  is the equilibrium velocity distribution given by Eq.(3.11) and

$$Q(T) = \sum_j \exp[-E(b,j)/T] \quad (4.5)$$

where the summation is over the assumed finite number of states.  $Q(T)$  is called the partition function and it depends on the temperature as well as on the way the different internal states of the system are distributed. Another way of expressing  $Q$  is

$$Q(T) = \sum^* g_j \exp[-E(b,j)/T] \quad (4.6)$$

where  $g_j$  is the number of different states with energy  $E(b,j)$  (that is the degeneracy of the state), and the summation (with the star) in Eq.(4.6) is now over distinct energies rather than over distinct states. The quantity  $g_j$  is also called the statistical weight of energy state  $E(b,j)$ . Thus the principle of detailed balance allows us to write the collision integral for the case of inelastic collisions in a way that the Maxwell Boltzmann statistics of the equilibrium can be derived. Alternatively, one might postulate Maxwell Boltzmann

statistics for the equilibrium, and use this to derive the principle of detailed balance for the particular kinetic theory studied.

Let us briefly consider  $Q(T)$ . It is a summation over all of the states or over all of the energy states multiplied by the statistical weight. The energies of the bound states are within some range from the minimum energy to the ionization energy. However because the Coulomb force is very long range, there are an infinite number of bound states. Thus the summation in Eq.(4.5) diverges if the summation is actually taken over all states. However there is some practical upper limit to the number of states. For instance for hydrogen atoms, the radius of an atom of principal quantum number  $p$  is roughly  $p^2 a_0$ , where  $a_0$  is the Bohr radius, about  $5 \times 10^{-9} \text{cm}$ . When this radius is about the interion separation,  $n_i^{-1/3}$ , the excited atom is no longer a distinct particle<sup>49</sup>. For an ion density of about  $10^{12} \text{cm}^{-3}$ , this is about the hundredth excited state. Furthermore, the ionization energy of this excited state is about 0.001ev, well below room temperature. Thus this excited state will surely ionize by interaction with the neighboring ion. (As discussed in Ref(49), there is little interaction between an excited ion and an atom whose wavefunction it overlaps, so the ion, rather than atom density is the appropriate density to use in calculating the maximum value of  $p$ .) Hence, for states above some maximum level, the excited states become in many ways indistinguishable from ionized states. This is the maximum excited state which the summation in Eq.(4.5) should be carried to. As long as the temperature is sufficiently below the minimum excitation energy, the fall off in the size of each term will compensate for any uncertainty in number of terms to retain. Equation (4.5) for the distribution of excited states is most accurate for low temperature where only a small number of excited states are relevant.

We digress briefly to discuss molecular plasmas. Here there are not only electronically excited states, but also rotational and vibrational states of the molecule. The calculation of the partition function and the associated partition of the molecules among these states must also be considered. Unlike the case of electronically excited states, there are only a finite number of rotational and vibrational states. When the rotational energy becomes too high, the rotation begins to interact with the inter nuclear vibration. The binding energy between the nuclei of the molecule is a short range force, so there are only a finite number of excited vibrational states of the molecule. To the extent that rotational, vibrational and

electronic states can be regarded as distinct, the partition function can be factored into rotational, vibrational and electronic factors. From this, one can determine the thermal equilibrium partition of molecular internal energy into these components<sup>49,50</sup>.

Let us now consider the ionization of the plasma at higher temperature still. Here we consider the equilibrium ionization. We now assume Maxwell Boltzmann statistics. If the ionized electron ion pair are considered to be an excited state with the ionization energy, an argument based on the Boltzmann statistics at equilibrium, and entirely analogous to that above, shows that the number of electrons, ions and atoms satisfies the relation:

$$N_e N_i / N_a = [\exp(-E_i/T)] G_e G_i / G_a \quad (4.7)$$

where  $E_i$  ionization energy and

$$G_a = \sum_j g_{ja} \exp \{-(E_{ja} - E_{0a})/T\} \quad (4.8)$$

for atoms and, with identical definitions for electrons and ions.  $E_0$  is the ground state energy for the species, and we have used the fact that

$$E_{0i} + E_{0e} - E_{0a} = E_i \quad (4.9)$$

The ionization process begins with a fixed atom and ion, but ends up with an extra free electron. Thus the key is to get the  $G$  factor for the additional free particle produced in the ionization (the electron). The electron has no internal structure, but it does have a spin, so there is a degeneracy factor of 2 from the spin. Now we calculate the  $G_e$  factor from the electron. Since the electron is free, it is highly degenerate and the  $G_e$  factor is quite large in nearly all cases. The electron is assumed to be in a system of length  $L$  confined in a volume  $V = L^3$ . It has wave function

$$\psi = \exp 2\pi i \mathbf{p} \cdot \mathbf{r} / h \quad (4.10)$$

and the boundaries impose the quantization condition  $p_x = nh/L$ , where  $n$  is an integer, and the number of free electron states within a velocity space volume  $d^3v$  is  $md^3vV/h^3$ . Integrating over all possible electron velocities with the assumed Boltzmann

distribution, and accounting for the spins of the electrons, we find that

$$G_e = 2V(2\pi mT)^{3/2}/h^3 \quad (4.11)$$

so that

$$n_e n_i / n_a = 2[2\pi mT/h^2]^{3/2} (G_i/G_a) \exp(-E_i/T) \quad (4.12)$$

using the fact that  $N_i/V = n_i$ . Equation (4.12) is the Saha Equation and it relates the ionization fraction to the temperature and the internal atomic structure at thermal equilibrium. Since for most atoms and ions,  $G_a = G_i$ , the Saha equation is often written without the G factors.

Now let us consider several of the ionization and recombination processes. There may be a great many, but we will consider only two for atomic systems; impact ionization and the reverse process of three body recombination, and photo ionization and the reverse process of radiative recombination. As we have seen in for instance Eq.(2.12), when averaged over the entire plasma, impact ionization can be written with as an ionization rate. Including the two ionization processes and their inverse processes, the equation for electron density can be written as

$$dn_e/dt = \alpha_i n_e n_a - \beta_i n_e^2 n_i + \alpha_p n_a I - \beta_p n_e n_i \quad (4.13)$$

In Eq.(.), the subscripts on the  $\alpha$ 's and  $\beta$ 's denote the impact and photon processes and I is the photon density. In thermal equilibrium,  $dn_e/dt$  must be zero, so this gives a relation between the  $\alpha$  and  $\beta$  coefficients. Because there are different functional dependences on production rate and loss rate depending on the process, in general there is no relation between say the different  $\alpha$ 's for the different processes. However there is always a relation between the  $\alpha$  and the  $\beta$  for the process and its inverse, as would be expected from the principle of detailed balance. This relation always gives the same functional relation between the densities. For instance, balancing impact ionization with recombination gives

$$n_e n_i / n_a = \alpha_i / \beta_i \quad (4.14)$$

while balancing photoionization with radiative recombination gives

$$n_e n_i / n_a = \alpha_p I / \beta_p \quad (4.15)$$

This is the same relation as long as  $\alpha_i / \beta_i = \alpha_p I / \beta_p$ . Of course these are not the same for any photon density  $I$ , however if one assumes that the photons are in thermal equilibrium at temperature  $T$ , then the ratios will be the same. Thus, at thermal equilibrium, the rate of the ionization process and its inverse are related by the Saha equation for all ionization processes.

To demonstrate the utility of the Saha Equation, we use it to calculate the rate of radiative recombination, which would otherwise be difficult, in terms of the rate of photoionization, which can be calculated analogously to the impact ionization, Eq.(2.12). The flux of photons at frequency  $\nu$  incident on an atom is the energy density at frequency  $\nu$  divided by  $h\nu$  times the group velocity  $c$ , the speed of light. The cross section for photoionization maximizes at the ionization energy and then falls off in frequency. We assume a frequency dependence of ionization cross section as  $\sigma_i = \sigma_0(\nu_i/\nu)^n$  for  $\nu > \nu_i$  and zero otherwise. The energy density of the electromagnetic radiation is given by the Planck spectrum

$$E(\nu) = [8\pi h\nu^3/c^3] \{ \exp(h\nu/T) - 1 \}^{-1} \quad (4.16)$$

Then one can do an asymptotic approximation to the integral in Eq.(4.16) to arrive at result

$$\begin{aligned} \alpha_p I &= [8\pi\sigma_0 E_i^2 T_e / c^2 h^3] \exp(-E_i/T_e) \\ &= 4 \times 10^{23} T(\text{eV}) E_i^2(\text{eV}) \sigma_0(\text{cm}^2) \exp(-E_i/T_e) (\text{s}^{-1}) \end{aligned} \quad (4.17)$$

for low values of  $T_e$ . Here  $E_i$  the ionization energy is  $h\nu_i$ . Then from the Saha Equation, we can determine the  $\beta_p$  coefficient as

$$\begin{aligned} \beta_p &= (8\pi\sigma_0 E_i^2) / [2(2\pi m)^{3/2} T_e^{1/2} c^2] \\ &= 65\sigma_0(\text{cm}^2) E_i^2(\text{eV}) / T_e^{1/2}(\text{eV}) (\text{cm}^3/\text{s}) \end{aligned} \quad (4.18)$$

From the fact the for photo ionization, typically  $\sigma_0 \approx 10^{-17} \text{ cm}^2$ , one can estimates rate of radiation recombination even for the case

where the radiation density is far below thermal equilibrium, the case for most processing plasmas.

While the ionization rate and recombination rate are, in all cases related by the Saha equation, this can at times be deceiving because the most important ionization and recombination processes might not be inverses of each other. Consider the case of three body recombination. Using Eq.(2.12) for the ionization rate and the Saha Equation, one would surmise that the recombination rate coefficient  $\beta$  is proportional to  $T_e^{-1}$ . However this three body recombination rate is the rate for recombination directly into the ground state with no intermediate radiative decays. Another reaction path is for the atom to recombine into a highly excited atomic state and then radiatively decay to the ground state. Because the highly excited state has a very large radius, as we have discussed, these cross sections can be very large. (Also the lifetime of these states to radiative decay is very short, so in a nonequilibrium plasma, ionization of these states will not be important.) Let us estimate the  $\beta$  coefficient for this process. At low temperature, two electrons which collide exchange energy of about  $T_e$ . The closest these electrons can get to each other is a separation  $e^2/T_e$ , and as they approach each other, one of them typically stops. If an ion is within this distance of the electron that nearly stops, the electron can form a highly excited bound state of the atom. The recombination rate then is the two particle collision cross section  $\pi e^4/T_e^2$  times the density of electrons  $n$ , times the relative electron velocity,  $(T_e/m_e)^{1/2}$ , times the probability that an ion is within the interaction region,  $\pi n(e^2/T_e)^6$ . By using the average radius of an excited atomic state, the quantum number squared times the Bohr radius; and the energy of the state compared to the continuum, the Bohr energy divided by the quantum number squared, we see that the state after collision is generally bound. Thus the three body recombination rate into highly excited atomic states is approximately

$$\beta(\text{cm}^6/\text{s}) \approx e^{10}/(m_e T_e^9)^{1/2} \approx 4 \times 10^{-27} T_e^{-9/2} (\text{eV}) \quad (4.19)$$

Thus for low temperature plasmas, the three body recombination rate via the formation of highly excited states can greatly exceed the direct three recombination rate into the ground state. Comparing Eqs.(4.18) and (4.19), we see that radiative recombination dominates three body recombination as long as

$$nT_e^{-4} < 10^{12}, \quad (4.20)$$

the usual condition for processing discharges. To derive Eq.(4.20), we have assumed  $E_i = 10$  eV and  $\sigma_0 = 10^{-17}$  cm<sup>2</sup>.

Whether the plasma is in thermal equilibrium or not will depend on the rates and densities as well as other properties of the plasma. For instance if the plasma boundary is transparent to photons and the optical depth of the plasma (the size of the plasma compared to the photon mean free path) is low (as is nearly always the case in processing discharges), the photon density could be well below its thermal equilibrium value. Also, at sufficiently low electron density and sufficiently high electron temperature, the radiative recombination can greatly exceed any three body recombination. If this is the case, the equilibrium density is determined by

$$n_i/n_a = \beta_p/\alpha_i \quad (4.21)$$

which is called coronal equilibrium. In coronal equilibrium, the fractional ionization depends only on the temperature. Actually, since impact ionization rate and radiative recombination rate depend on the relative velocity of the atom or ion with the electron, the coronal equilibrium condition does not necessarily depend on the plasma being in thermal equilibrium. If the electron temperature is much greater than the ion temperature, as is usually the case in processing discharges, the coronal equilibrium depends only on the electron temperature, since the electrons are the controlling species.

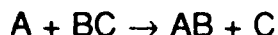
Processing discharges are rarely in thermal equilibrium. In fact, because the electron (and therefore ion) density is usually very low, it is not often that recombination is an important process at all. More often, impact or photo ionization, or ionization from the impact of fast particles on the wall are the important processes, and the loss mechanism is governed by diffusion, convection, or recombination at the walls. As is apparent from Eq.(4.13), the various electron production and loss terms depend on different powers of the density. Hence for low density, only those terms having the lowest power of density will play a role at all. In fact diffusion, which is not included in Eq.(4.13), but whose loss rate is

linear in density will often be the dominant loss mechanism. From the knowledge that a process and its inverse drive the system to thermal equilibrium, we can calculate the coefficient for one of the processes if that for the inverse process is known. From this knowledge, one can estimate the density regimes for which the plasma will tend to thermal equilibrium. This will occur at sufficiently high density.

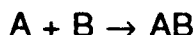
## 5. Homogeneous, Molecular Plasmas

Processing plasmas are not usually atomic plasmas, atomic argon plasmas are used in sputtering. The fact that the plasma is molecular gives rise to chemistry, as well numerous rotational and vibrational internal states which would figure in the energy equation of the gas species. In this section we will discuss only the chemistry of one of the simplest molecular plasmas, an oxygen plasma. In a processing discharge, an oxygen plasma is important because it is a source of atomic oxygen, a very reactive free radical. We start with a discussion of a low density plasma with hot electrons and cool gases and ions; the type usually found in processing discharges. Many of the reactions rates are as given in Talrose and Karachevtsev<sup>51</sup>.

One thing about a processing discharge is that the chemistry is usually dominated by the free electrons. The reason is that the rate of a chemical process goes as  $\alpha = \int \sigma v f(v) d^3v$ , so that the electrons, with their lighter mass and higher temperature give rise an  $\alpha$  which is  $(T_e M / T_g m)^{1/2}$  larger than a that of the gas if the cross sections are equal. We also consider low density plasmas, so that the chemistry is mostly through two particle collisions. The typical reaction is then something like



and these usually have high reaction rate. An alternate possible two body reaction like



is usually less important because some third body not shown there is necessary for momentum and energy conservation, a photon typically. For instance one potential such process is radiative recombination, whose reaction rate was calculated in the last section. At temperatures of a few electron volts, the reaction rates are about  $10^{-13}$  cm<sup>3</sup>/s, far smaller than other rates we will consider here. Another possible chemical reaction,  $O + O \rightarrow O_2$  is also typically not important in a processing plasma. Such a reaction proceeds by the  $O_2$  forming a positive energy excited state. Then it decays to a negative energy state by either radiation or interaction with another oxygen atom or molecule. For the former, the decay

time (that is the redissociation time) of the excited state is much less than the radiative decay time, so the reaction through this channel has very low rate. The other channel is through interaction with a third body oxygen atom or molecule, which is a three body process, which we assume is negligible at the low densities considered. However if the third body is the wall of the chamber, atomic oxygen can easily recombine. thus surface reactions can be a whole new reaction set.

Let us then consider the two body reactions in an oxygen plasma. We will consider 6 species,  $O_2$ ,  $O$ ,  $O_2^+$ ,  $O^+$ ,  $e$ , and  $O^-$ , whose densities we will denote  $a, b, c, d, e$  and  $f$ . Note that even this is restrictive, because we are not considering excited states of the oxygen. However, even with this restricted set, there are a very large number of possible reactions. The principle reactions seem to be:

Ionization:



described by Eq.(2.12) with an ionization energy of 12 eV and a maximum ionization cross section of  $3 \times 10^{-16} \text{ cm}^2$ , and.



with  $E_i = 15 \text{ eV}$ ,  $\sigma_0 = 3 \times 10^{-16} \text{ cm}^2$ ;

Dissociative ionization:



with  $E_i = 20 \text{ eV}$  and  $\sigma_0 = 10^{-16} \text{ cm}^2$ . Cross sections for these processes are given in Ref(51);

Dissociation:



described by Eq.(2.12) with  $E_i = 8 \text{ eV}$ ,  $\sigma_0 = 10^{-16} \text{ cm}^2$ . This expression agrees to within about a factor of two to that given in Ref.(51) p126.

### Dissociative Recombination:



Assuming a dissociative recombination cross section as  $\sigma = 4 \times 10^{-16}/E$  for  $E < 3\text{ eV}$  and zero otherwise (here and in all formulae, energies are in eV and lengths are in cm) the dissociative recombination rate is given roughly by  $(2.6 \times 10^{-8}/\sqrt{T_e})[1 - \exp(-3/T_e)]$  in  $\text{cm}^3/\text{s}$

### Dissociative attachment:



This depends on the vibrational state of the molecule. For gas temperatures below about  $1000^\circ\text{K}$ , the gas is not strongly excited and the attachment cross section peaks at about  $10^{-19}\text{ cm}^2$  for energies between about 5 and 8 eV. The attachment rate is given by roughly  $(6.4 \times 10^{-12}/\sqrt{T_e}) \times [(5/T_e + 1)\exp(-5/T_e) - (8/T_e + 1)\exp(-8/T_e)]$ . Although the rate of dissociative attachment is small, it is the largest production rate for negative oxygen ions. Furthermore, while the rate is small, if the plasma is weakly ionized, it multiplies the concentration of  $O_2$ , the largest concentration.

### Electronic detachment:



The minimum electron energy for detachment is about 7 eV and above this energy, the cross section is about  $7 \times 10^{-16}$ . This gives a detachment rate of  $3 \times 10^{-7} T_e^{-1/2} \exp(-7/T_e)$ .

### Associative detachment:



The rate for this process is given as  $3 \times 10^{-10}$  in ref (51) p.110. Since it is strictly an atomic process, it does not depend on the electron temperature. Ion-molecule reactions can have large cross sections even without involving an electron component because the ion can polarize the target molecule, thereby giving rise to a very

large reaction cross section. If both are charged, the reaction rate can be even higher, as in

Positive-negative charge exchange:



Reference 51 , page 115 quotes a reaction rate of  $10^{-7}$  for the reaction of nitrogen and oxygen. We assume that rate here.

Thus, even for this relatively simple system of oxygen and nothing else, we have identified nine important reactions; there are undoubtedly many other important ones left out, especially the many involving the vibrationally excited states oxygen. Below we enumerate the processes and the approximate reaction rate in  $\text{cm}^3/\text{s}$  at an electron temperature of 3 ev, a typical temperature for a processing discharge. We denote the reaction rate by  $\alpha_i$  where  $i$  denotes the equation number 5.1-5.9

| Process    | Rate in $\text{cm}^3/\text{s}$ |
|------------|--------------------------------|
| $\alpha_1$ | $10^{-9}$                      |
| $\alpha_2$ | $3 \times 10^{-10}$            |
| $\alpha_3$ | $3 \times 10^{-10}$            |
| $\alpha_4$ | $3 \times 10^{-9}$             |
| $\alpha_5$ | $6 \times 10^{-9}$             |
| $\alpha_6$ | $3 \times 10^{-12}$            |
| $\alpha_7$ | $1.7 \times 10^{-8}$           |
| $\alpha_8$ | $3 \times 10^{-10}$            |
| $\alpha_9$ | $10^{-7}$                      |

In a weakly ionized processing plasma with low gas temperature, and electron temperature in the ev range, all of the reactions proceed only in the forward direction. The reverse reactions, in all cases (except for 6 and 8 which of course are reverse reactions of each other) have an energy threshold that the heavy particles cannot get over, or are three body reactions which do not proceed at low density.

The rate of change of the six quantities are then determined by the six equations describing the reactions.

$$a' = -(\alpha_1 + \alpha_3 + \alpha_4 + \alpha_6)ae + \alpha_8fb \quad (5.10)$$

$$b' = (-\alpha_2b + \alpha_3a + 2\alpha_4a + \alpha_5c + \alpha_6a + \alpha_7f)e - (\alpha_8b - \alpha_9d)f \quad (5.11)$$

$$c' = (\alpha_1a - \alpha_5c)e \quad (5.12)$$

$$d' = (\alpha_2b + \alpha_3a)e - \alpha_9df \quad (5.13)$$

$$e' = (\alpha_1a + \alpha_2b + \alpha_3a - \alpha_5c - \alpha_6a + \alpha_7f)e + \alpha_8bf \quad (5.14)$$

$$f' = \alpha_6ae - (\alpha_7e + \alpha_8b + \alpha_9d)f \quad (5.15)$$

where a prime indicates a derivative with respect to time. It is simple to verify that the reactions (5.10-5.15) together conserve charge as indeed they must.

Since a processing plasma is in steady state, a natural question is whether the steady state constituents of a processing plasma can be determined from the chemistry alone once the reaction rates (that is the electron temperature) are specified. Although some quantities may have steady state densities determined through the chemistry, in general the answer is no. We now demonstrate each case. Consider first the case of  $O^-$ . There is only one source of it, dissociative attachment, and three loss channels. In steady state,

$$f = \alpha_6ae / (\alpha_7e + \alpha_8b + \alpha_9d) < 2 \times 10^{-4}a \quad (5.16)$$

If the fractional ionization is greater than about  $10^{-4}$ , the  $O^-$  number density is small compared to the all other ion densities, particularly if  $d=e$ . However the decay time for  $O^-$  to reach equilibrium is less than  $(2 \times 10^{-8} d)^{-1}$  seconds, so at electron densities of  $10^{10}$ , the decay time is small enough that equilibrium could be reached for  $O^-$ . Normally this equilibrium would result in a very low value of  $O^-$ . Thus, for the other rate equations, we make the approximation  $f=0$ . In this case, it is clear that there can be no equilibrium for  $a$ , because there are only loss terms. Similarly in the electron equation, all terms are source terms except the  $\alpha_5$  and  $\alpha_6$  terms. The former has a high rate, but it is multiplied by  $c$ , the number density of  $O_2^+$ , which is much less than  $a$  for weakly ionized plasma. The latter has a very low rate. Thus these two terms are small compared to the others, so effectively, the equation for  $e$  has only production terms and cannot reach an equilibrium density. Equation (5.12) for  $c$  looks like it could reach an equilibrium, however the equilibrium value is  $c=(\alpha_1/\alpha_5)a=a/6$ . Thus the equilibrium fractional ionization predicted by the rate equations is huge, much greater than what is observed in processing discharges. Hence the inescapable conclusion is that chemistry alone does not determine the steady state components of the discharge. As we will see in a later section, it is chemistry coupled to the fundamental discharge processes which determine the composition.

We now consider briefly the opposite extreme, a molecular plasma at thermal equilibrium. Here, all species (including the radiation) are at a given temperature  $T$ . Because the dense background gas is at this temperature rather than the cooler gas temperatures characteristic of processing discharges, the equilibrium plasma is usually much more energetic, even though the temperature is typically less than that of the electrons in a processing discharge. Typical temperatures might be under 1 ev. In thermal equilibrium, the reverse reactions cannot be neglected, in fact thermal equilibrium is defined by a balance between forward and reverse reactions which are satisfied for all possible reactions.

Let us consider the reactions we have just discussed for an oxygen plasma, except let us make the additional simplification of neglecting the  $O^-$ . Then there are 5 reactions with forward reaction rate  $\alpha_1-\alpha_5$ . However at thermal equilibrium, the reverse reaction can also occur, and we define the rates of the reverse reactions as  $\beta_1-\beta_5$ . The reactions and the reverse reactions all conserve charge

and mass, so  $e=c+d$  and  $a+2b+c+2d=A$ , the total number of oxygen nuclei. Setting each reaction at equilibrium, we find five equilibrium relations

$$\alpha_1 a = \beta_1 e c \quad (5.17)$$

$$\alpha_2 b = \beta_2 e d \quad (5.18)$$

$$\alpha_3 a = \beta_3 e b d \quad (5.19)$$

$$\alpha_4 a = \beta_4 b^2 \quad (5.20)$$

$$\alpha_5 e c = \beta_5 b^2 \quad (5.21)$$

The five conditions specified plus the conservation relations would appear to over specify the system. However this is not so, because the equations are not all independent. For instance  $a$  can go to 2  $b$ 's directly via equation (5.20). However alternatively it can go to 2  $b$ 's by first going through an intermediate stage of an  $e$  and  $c$ , Eq.(5.17); and then the  $e$  and  $c$  react to give 2  $b$ 's. Thus there must be a relationship between the rates of the two reaction channels of getting from the  $a$  to the two  $b$ 's. Specifically, we must have  $\beta_4/\alpha_4 = \beta_1\beta_5/\alpha_1\alpha_5$ . Thus reaction with rate  $\alpha_4$  is not independent in the sense that its rates are determined by other reactions by the principle of detailed balance. We can also show that reactions (5.18) and (5.19) are not independent either, and the coefficients must satisfy the relationship  $\alpha_3\beta_2/\alpha_2\beta_3 = \alpha_4/\beta_4$ . Letting the three independent reactions be those with index 1,2 and 4, and using the conservation relations, we find

$$(c+d)c/(A-2b-c-2d) = \beta_1/\alpha_1 \quad (5.22)$$

$$b^2/(A-2b-c-2d) = \alpha_4/\beta_4 \quad (5.23)$$

$$(c+d)d/b = \alpha_2/\beta_2 \quad (5.24)$$

Since  $A$ , the total concentration is arbitrary, we have three equations for the three independent variables  $b$ ,  $c$ , and  $d$ . Thus at thermal equilibrium, the reaction rates between the independent forward and reverse reactions determine the equilibrium

concentrations of all quantities in terms of the total number density and the equilibrium temperature.

For the reactions enumerated here, the temperature is generally low compared to the various ionization rates. In this case, it is only the tail of the distribution function that does the ionizing. As in many of the preceding calculations, the reaction rates for those reactions requiring a minimum energy  $E_j$  will have a rate like  $f(T)\exp(-E_j/T)$ , where here  $j$  denotes the reaction and takes on values from one to five in the oxygen plasma we consider here, and  $f(T)$  is a slowly varying function of  $T$ . While this form is particularly useful for  $E_j \gg T$ ; it is still valid for  $E_j \approx T$ , but is not very meaningful since in this limit, the exponential is no longer a rapidly varying function of  $T$ . The first four reactions all take a minimum energy to proceed in the forward direction. These are the ionization energy of the oxygen molecule, 12 ev; the ionization energy of the oxygen atom, 15 ev; the dissociative ionization energy of the oxygen molecule, 20 ev; and the dissociation energy of the oxygen molecule, 8 ev. Thus the  $\alpha$ 's for the first four will have this exponential factor. The fifth reaction takes energy to proceed in the reverse direction. When the oxygen atoms form the molecule, they lose an energy to 8 ev in the center of mass frame. However it takes 12 ev to ionize the molecule, so the colliding oxygen atoms need at least an energy of 4 ev in the center of mass frame. Thus it is  $\beta_5$ , not  $\alpha_5$ , that will be multiplied by the exponential factor.

## 6. Scaling Laws for Binary Collisional Plasmas

We consider the case of a processing discharge consisting of three components, electrons (index e), ion (i), and neutrals (n). These species may have internal structure, however to simplify the notation we will not introduce additional indices to account for it as we did in the previous section. Nevertheless we include in our description all ionization and excitation processes. The main assumptions we make are that the plasma density is sufficiently low that only binary collisions are included, and also that the plasma is optically thin so all radiation escapes and has density much less than thermal equilibrium radiation density. Notice that thermal equilibrium ionization densities would occur only by chance since the inverse processes to impact ionization and radiative recombination are not included in the model. However for most low density processing discharges, these assumptions are valid.

The plasma is described by the Vlasov Equation for the three species coupled to Maxwell's Equation.

$$\partial f_a / \partial t + \mathbf{v} \cdot \nabla f_a + (e_a / m_a) [\mathbf{E} + \mathbf{v} \times \mathbf{B} / c] \cdot \nabla_v f = \sum_b C_{ab} \quad (6.1)$$

$$\nabla \times \mathbf{B} = (4\pi / c) \sum_b n_b e_b \mathbf{v}_b + (1/c) \partial \mathbf{E} / \partial t \quad (6.2)$$

$$\nabla \cdot \mathbf{E} = 4\pi \sum_b n_b e_b \quad (6.3)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (6.4)$$

$$\nabla \times \mathbf{E} = -(1/c) \partial \mathbf{B} / \partial t \quad (6.5)$$

The quantities  $n$  and  $n\mathbf{v}$  are the first and second velocity integral of the appropriate distribution function. These equations cannot be solved analytically. However in some cases there are scaling laws that which allow the solutions in one regime to be extended to another. We consider only scaling within an atomic species. If one goes from species to species (an oxygen to argon plasma for instance), there are some simple scalings with mass as that explicitly shown on the left hand side of Eq.(6.1). However collision cross sections for all the multitude of possible processes depend very much on the atomic species and there is no simple scaling law

from one to another. Similarly, we consider only scaling laws that leave particle velocity (and therefore energy and temperature) constant. Cross sections often have complicated velocity dependences for which there is no simple scaling. Furthermore, experimentally, all processing plasmas have temperatures of a few electron volts, whereas there can be a wide range of densities as well as spatial and temporal scales.

The collision terms are quadratic in distribution function. If we consider a scaling transformation of the form

$$f' = p^a f, t' = p^b t, x' = p^c x, v' = v, E' = p^e E, B' = p^f B \quad (6.6)$$

it is not difficult to see that there are no choices of exponents (a,b,c,e and f) which leave equations (6.1-6.5) invariant. Thus there is no general scaling law for a processing plasma. However there are scaling laws that are consistent with certain approximations to these equations. As one possibility, let us assume that the plasma is quasi-neutral (more about quasi-neutrality in Section (8)), and that the plasma currents are so small that they do not contribute in a significant way to the magnetic fields. Then Eq.s (6.2 and 6.3) are replaced with

$$\sum_b n_b e_b = 0 \quad (6.7)$$

$$\nabla \times \mathbf{B} = (1/c) \partial \mathbf{E} / \partial t \quad (6.8)$$

In this case there is a scaling law,

$$a=e=f=1, b=c=-1 \quad (6.9)$$

This shows that if one solution (subject to this approximation) is known, the densities of all species can be increased by a factor p as long as all fields are increased by this same factor and lengths and times (inverse of driving frequencies for instance) are decreased by this factor.

Another approximation is that the plasma is collisionless so that the right hand side of Eq.(6.1) vanishes. In this case another scaling law exists

$$a=2, e=f=1, b=c=-1 \quad (6.10)$$

Thus the density densities now increase as the field strength squared in the scaled solution.

In processing discharges, usually neither of these approximations are valid over the entire discharge. However one or the other may be valid in large portions of it. As we will see, the main volume of the plasma is quasi-neutral, so that the scaling laws of Eq.(6.9) can be used to scale from one density regime to another. In particular, for a discharge generated by a DC electric field, the density (or operating pressure) divided by the electric field is the same as the discharge is scaled from one regime to another. Thus  $E/p$  is a commonly used parameter in discharge plasmas. However this is not an invariant quantity if the plasma allows charge separation. We will see shortly that processing discharges, the plasma near a surface is dominated by sheaths in which quasi-neutrality is strongly violated. In fact these sheaths are what generate the fast ions and atoms that are important for the etching, sputtering, ion implantation, etc. Since they are such a crucial part of the processing discharge,  $E/p$  is generally not an important parameter for the entire processing discharge, but only for that region in the center which is quasi-neutral.

## 7. Fluid Equations for Processing Plasmas

This section derives fluid equations for the components of a processing discharge. To simplify the derivation, we assume only a single atom for the background fluid and the associated singly ionized ion. There are then three species in the plasma which we denote with subscripts a, e and i. The Vlasov equation for each species is given by Eq.(3.1). Three fluid equations for number density, momentum density and energy density are obtained for each species. These are obtained by integrating the Vlasov Equation over velocity, and multiplying by momentum and energy and then integrating over velocity.

The fundamental difficulty is that each moment is coupled to the next higher moment by the  $\mathbf{v} \cdot \nabla f$  term in the Vlasov Equation. The hierarchy of fluid equations can only be closed by making some sort of approximation. A typical one, one made in Ref.(5) is that the distribution function of each species is approximately a local Maxwellian. If each species had the same fluid velocity and temperature and the system were homogeneous, this would be an exact solution to the Vlasov Equation. However it is not a solution to the Vlasov Equation for two reasons; first, the velocities and temperatures of the components may be different, and second, the system can be inhomogeneous and time dependent. The effect of the different velocities and temperatures is an energy and momentum exchange between the components as described in Sec 2. The effect of the inhomogeneity is the introduction of transport. We will consider these two processes separately.

To start, we will assume that the distribution of the species in question is a Maxwellian and there are no internal energy states, that is an atomic plasma with all atoms in the ground state. If the fluid velocity of the species in question is  $\mathbf{u}$ , the particle velocity in Vlasov equation is given by  $\mathbf{u} + \mathbf{w}$ , so  $\mathbf{w}$  is the random velocity about the average. Where convenient, to keep the notation as simple as possible, we will delete subscripts denoting species. Where necessary we will return to using them. Then integrating the Vlasov Equation over velocity and multiplying by  $m\mathbf{v}$  and integrating over velocity, we find two equations for number density and momentum:

$$\partial n / \partial t + \nabla \cdot n \mathbf{u} = M_c \quad (7.1)$$

$$\partial n m \mathbf{u} / \partial t + \nabla \cdot [n m \mathbf{u} \mathbf{u} + n \mathbf{T}] - n e \mathbf{E} - n e [\mathbf{u} \times \mathbf{B}] / c = \mathbf{P}_c \quad (7.2)$$

The charge  $e$  is the charge of the species in question with the appropriate sign, that is, it would have a subscript. Here,  $M_c$  and  $P_c$  are the collisional rates of change of number density and momentum density. The former comes from for instance ionization and recombination, the latter from momentum exchange between the different species as well as ionization and recombination. Often it is convenient to combine Eqs.(7.1 and 7.2) to give an equation for the acceleration of the plasma species:

$$n m \partial \mathbf{u} / \partial t + n m \mathbf{u} \cdot \nabla \mathbf{u} + \nabla n T - n e \mathbf{E} - n e [\mathbf{u} \times \mathbf{B}] / c = \mathbf{P}_c - m \mathbf{u} M_c \quad (7.3)$$

For the energy equation, we will consider the electrons and ions separately. For the electrons, multiplying the Vlasov Equation by  $1/2 m v^2$  and integrating over velocity, we find an equation for the energy is

$$\begin{aligned} \partial / \partial t [1/2 n m u^2 + 3/2 n T] + \nabla \cdot [1/2 n m u^2 \mathbf{u} + 5/2 n \mathbf{u} T] \\ - n e \mathbf{u} \cdot \mathbf{E} = W_c \end{aligned} \quad (7.4)$$

where  $W_c$  is the collisional rate of change of energy density. The total electromagnetic energy input into the fluid is the electric field dotted into the current density of the species, as is to be expected. This can also be written as a temperature equation by subtracting  $\mathbf{u}$  dotted into the momentum equation and adding  $1/2 m u^2$  times the number density equation. The result is

$$3/2 \partial n T / \partial t + 3/2 \mathbf{u} \cdot \nabla n T + 5/2 n T \nabla \cdot \mathbf{u} = W_c - \mathbf{u} \cdot \mathbf{P}_c + 1/2 m u^2 M_c \quad (7.5)$$

Notice that in Eq.(7.5) above, the electric field no longer appears. The Ohmic heating is now expressed as a collisional heating. In equations (7.1-7.5), we emphasize that the assumption has been explicitly made that the species has a Maxwellian velocity distribution with temperature  $T$  and velocity  $\mathbf{u}$ . Thus the collision term for the interaction of the species with itself vanishes; the collision terms  $M$ ,  $P_c$  and  $W_c$  describe changes in number density, momentum and energy from the interaction of one species with an other species in the plasma having different drift velocity and temperature.

The ions can be more complicated because they can have internal energy states. Molecules can have rotational and vibrational states. At thermal equilibrium, the internal energy of the ions over the internal states is governed by the partition function, as discussed in Sec 4 and Ref.(50). However, low density processing plasmas are almost never in thermal equilibrium because the electrons are at much higher temperature than the ions or neutrals. In this case the internal energy must be obtained in some other way, perhaps by some approximation, or perhaps by solving rate equations for the internal states regarded as important. We will not consider this here, but will discuss atomic plasmas. Again, we will not consider the internal states of the atom, but there is one state that cannot be wished away and that is the ionization. Since it takes significant energy to ionize the atom, this energy must be accounted for. If the ionization energy is  $E_i$ , each ion will be considered to have an internal energy  $E_i$ . In the simplest description, it takes energy  $E_i$  to produce this ion. Actually, since ionization can occur in multistep processes, where some of the intermediate steps radiate away their energy, the actual energy it takes to produce an ion can be larger than  $E_i$ , but we will simplify the description by taking  $E_i$  to be the entire energy involved in the ionization. In this case, we will assume that each ion has an internal energy  $E_i$ . Then the temperature equation for atomic ions becomes

$$\begin{aligned} 3/2 \partial(nT + nE_i)/\partial t + 3/2 \mathbf{u} \cdot \nabla nT + E_i \nabla \cdot n\mathbf{u} + 5/2 nT \nabla \cdot \mathbf{u} = \\ W_c - \mathbf{u} \cdot \mathbf{P}_c + 1/2 m u^2 M_c \end{aligned} \quad (7.6)$$

Let us first discuss the momentum exchange, that is the force between the different species. The average force is given by Eq.(2.7). It is not difficult to show, that the momentum integral of the Boltzmann collision integral can be reduced to this form. We focus here on the average force between the electrons, the main current carriers in processing plasmas; and the atoms, the main target of electron collisions since the fractional ionization is typically low. For electron atom collisions, we assume that  $w_e \gg u_e, u_a, w_a$  and expand relative velocities based on this scaling. Defining  $n_a w_e \sigma_p(w_e)$  as the electron momentum exchange collision frequency,  $\nu_p(w_e)$ , Eq.(2.7) can be expanded in a power series. Keeping only the first few terms, we find

$$\begin{aligned} \mathbf{P}_{ea} = & -\mu \int d^3\mathbf{w}_a d^3\mathbf{w}_e \{ \mathbf{w}_e v_p(\mathbf{w}) + (\mathbf{u}_e - \mathbf{w}_a - \mathbf{u}_a) v_p(\mathbf{w}_e) \\ & + \mathbf{w}_e \partial v_p / \partial \mathbf{w}_e [\mathbf{u}_e - \mathbf{w}_a - \mathbf{u}_a] \cdot \mathbf{w}_e \} / w \} f_e f_a \end{aligned} \quad (7.7)$$

where the notation  $\mathbf{P}_{ea}$  means the average force, or momentum exchange between electrons and atoms. The integral of the first term in the brackets is zero because of the assumed Maxwellian nature of  $f_e$ . (Actually isotropy about the drift velocity is a sufficient condition for the vanishing of this term. However if the distribution function is anisotropic for any reason, for instance the presence of a viscous momentum flux, or thermal energy flux, this term will no longer integrate to zero over  $\mathbf{w}_e$ . These are thermal flux force terms for instance. We will not consider them here.) In the simplest case, where  $v_p(\mathbf{w}_e)$  is independent of  $\mathbf{w}_e$ , the Force term is particularly simple. It is

$$\mathbf{P}_{ea} = -n_e \mu [\mathbf{u}_e - \mathbf{u}_a] v_p = -\mathbf{P}_{ae} \quad (7.8)$$

Since  $v_p$  is proportional to  $n_a$ , the force density has appropriate symmetry between the species. For convenience, we will sometimes use the definition  $v_p(\mathbf{w}_e) \equiv n_a \theta_p(\mathbf{w}_e)$ .

For elastic collisions, the energy density exchange between species is given by Eq.(2.9). Again, one can show that an integral of the Boltzmann collision integral gives this result. Expressing the  $\mathbf{v}$ 's in terms of the  $\mathbf{w}$ 's and  $\mathbf{u}$ 's, we find

$$\begin{aligned} W_{ea} = & -k \int d^3\mathbf{w}_e d^3\mathbf{w}_a n_e n_a f_e f_a \theta_p [m \mathbf{w}_e^2 + 2m \mathbf{w}_e \cdot \mathbf{u}_e + m \mathbf{u}_e^2 - M \mathbf{w}_a^2 - \\ & 2M \mathbf{w}_a \cdot \mathbf{u}_a - M \mathbf{u}_a^2 + (m-M)(\mathbf{u}_e + \mathbf{w}_e) \cdot (\mathbf{u}_a + \mathbf{w}_a)] \end{aligned} \quad (7.9)$$

Here we have used  $m$  and  $M$  for the electron and atom mass respectively. Also, we have made the simplifying assumption that  $\theta_p$  is independent of  $\mathbf{w}$  as we did for the momentum equation. The integrals over  $\mathbf{w}$  can now be done assuming Maxwellian distribution functions. In addition to the elastic collisions, there is a significant energy loss from inelastic collisions. The only inelastic collision process we consider is impact ionization. This causes a loss of energy  $E_i$  from each electron doing the ionizing, and a corresponding gain of internal ion energy of this amount.

$$W_{ea} = -kn_e v_p [3(T_e - T_a) + (mu_e + Mu_a) \cdot (u_e - u_a)] - E_i M_c \quad (7.10)$$

Of this total electron energy loss, the elastic part goes into to the neutral gas, so

$$W_{ae} = kn_e v_p [3(T_e - T_a) + (mu_e + Mu_a) \cdot (u_e - u_a)] \quad (7.11)$$

and the contribution to the electron ion energy exchange is  $E_i M_c$ .

Notice that there are two contributions to the elastic energy exchange term, one driven by the temperature difference between the two species, and one driven by the relative velocity between them. Notice that in the limit of  $m \ll M$ , the  $W$  term approaches zero in the reference frame in which the atoms are at rest. This is reasonable, because in this limit, the electrons bounce off infinitely massive, fixed scattering centers, which do not absorb from, or contribute energy to the electron in an elastic collision. To next order in  $m/M$ , there is a temperature equilibration whose rate is  $-3(m/M)n_e v_p (T_e - T_a)$ . For the case in which the electron thermal velocity is much greater than the electron drift velocity  $u$ , the other terms in  $W_{ea}$  are less important. However the electron thermal energy equation, Eq.(7.5) has a heating term equal to  $-u \cdot P_c$ . Thus collisions take energy out of drift motion and put it into thermal energy. The second term in Eq.(7.11) above is an order  $m/M$  correction to this electron heating. The momentum and energy exchange terms derived here are convenient approximations, but only that, because the velocity dependence of  $\theta$  as well as most internal energy states were neglected.

We now consider the case of transport. This gives rise to terms in the fluid equation which result from the fact the the actual distribution function deviates from the local Maxwellian. As we will see, deviations from a Maxwellian are produced by gradients and time dependences in the plasma. Typically we consider gradients to be a more important effect than the time dependence. A method of deriving an augmented set of fluid equations is to assume that the distribution function consists of a Maxwellian times a summation of various products of velocity. This is the approach taken in Refs.(.). For instance a distribution which had a non zero component of momentum flux (other than the scalar pressure of course) would be something like  $w w f_m$  where  $f_m$  is the Maxwellian. We consider only a single transport coefficient here, thermal electron energy flux. A

distribution function can be written which has a non zero energy flux vector,  $\mathbf{q} = \int d^3w \frac{1}{2} m w^2 \mathbf{w} n f \neq 0$ . For a Maxwellian distribution function,  $\mathbf{q} = 0$ , so no term from  $\mathbf{q}$  appears in the fluid equations as they have been written so far. If  $\mathbf{q} \neq 0$ , then in the energy density equation, there is an additional term  $\nabla \cdot \mathbf{q}$  on the left hand sides of Eqs.(7.5 or 7.6). The trick then is to find  $\mathbf{q}$  in terms of fluid quantities.

Following the logic of Refs.(), we assume an electron distribution function

$$f = f_m [1 - \mathbf{q} \cdot (m \mathbf{w} / n T^2) (1 - m w^2 / 5 T)] \quad (7.12)$$

where  $f_m$  is a Maxwellian for the electrons with Temperature  $T$  and flow velocity  $\mathbf{u}$ . The additional term does not contribute to the density or the temperature because it is an odd function of  $\mathbf{w}$ . The coefficients of the two terms in the brackets were chosen so that it does not contribute to the fluid velocity either. That is if  $\mathbf{v} - \mathbf{u}$  is substituted for  $\mathbf{w}$ , the fluid velocity will still come out to be  $\mathbf{u}$ . The lowest nonzero moment of the assumed distribution function is the thermal energy flux, which comes out to be equal to  $\mathbf{q}$ .

To determine an equation for  $\mathbf{q}$ , we take the  $\frac{1}{2} m v^2 \mathbf{v}$  moment of the Vlasov Equation. The first term (the  $\partial/\partial t$  term) is relatively straightforward to calculate. It is

$$\partial/\partial t [1/2 n m u^2 \mathbf{u} + 5/2 n T \mathbf{u} + \mathbf{q}]$$

The second term (the  $\mathbf{v} \nabla f$  term) is more complicated. To write the term in simplest form, we make assume that  $m u^2 \ll T$  and also that  $m u q \ll n T^2$ . Making this approximation, we find that this term becomes  $5/2 \nabla n T^2 / m$ . Upon several straightforward partial integrations and vector manipulations, the electric field term becomes

$$-n e \mathbf{u} \cdot \mathbf{E} - 1/2 n e u^2 \mathbf{E} - 5/2 (e \mathbf{E} / m) n T$$

The magnetic term is the most burdensome of all to evaluate. It turns out to be

$$-[5/2(neT/mc) + 1/2(neu^2/c)]\mathbf{u} \times \mathbf{B} - (e/mc)\mathbf{q} \times \mathbf{B}$$

This involves a fair number of vector identities and symmetries of  $\mathbf{f}$  and  $\mathbf{f}_m$ . In evaluating integrals over cross products in the terms leading to the  $\mathbf{q} \times \mathbf{B}$  term, it is often convenient to express cross products in terms of tensor notation  $(\mathbf{a} \times \mathbf{b})_i = \epsilon_{ijk} a_j b_k$  where  $\epsilon_{ijk}$  is the completely antisymmetric third rank tensor having  $\pm 1$  as the nonzero elements.

Thus the energy flux equation becomes

$$\partial/\partial t [1/2 n m u^2 + 5/2 n T u + \mathbf{q}] + 5/2 \nabla n T^2 / m$$

$$- n e u (\mathbf{u} \cdot \mathbf{E}) - 1/2 n e u^2 \mathbf{E} - 5/2 (e \mathbf{E} / m) n T -$$

$$[5/2 (n e T / m c) + 1/2 (n e u^2 / c)] \mathbf{u} \times \mathbf{B} - (e / m c) \mathbf{q} \times \mathbf{B} = \mathbf{Q}_c \quad (7.13)$$

where  $\mathbf{Q}_c$  is the energy flux integral of the Boltzmann collision term. This can be simplified further by using the mass, momentum and energy equations to manipulate the left hand side of Eq.(7.13) into a form in which the terms that do not involve  $\mathbf{q}$  are subtracted out from the left hand side. The result is

$$\partial \mathbf{q} / \partial t + 5/2 (n T / m) \nabla T - (e / m c) \mathbf{q} \times \mathbf{B} = \mathbf{Q}_c - \mathbf{P}_c [5/2 T / m + 1/2 u^2]$$

$$- 5/3 \mathbf{u} (\mathbf{u} \cdot \mathbf{P}_c) + 5/3 \mathbf{u} W_c + M_c [5/2 \mathbf{u} T - 1/6 m u^2 \mathbf{u}] \quad (7.14)$$

From the collision terms on the right hand side of Eq.(7.14), one can track how the various fluid equations were multiplied by fluid quantities and added or subtracted from the momentum flux equation. In arriving at Eq.(7.14), it is necessary to drop terms in the spatial gradient term which are small by factors like  $\mu u^2 / T$  or  $\mu u q / n T^2$ . That is the flow velocity and energy flux velocity are all assumed small compared to the electron thermal velocity.

We now deduce an approximate evaluation of the right hand side of Eq.(7.14) so as to derive a fluid equation for  $\mathbf{q}$ . In a weakly ionized plasma, the main electron collision process is with the background ions. We assume that the background gas consists of atoms of infinite mass compared to the electrons which are at rest. Thus the electrons perform purely elastic scatter from fixed sites. If we make the same simplifying assumption as before, namely that

the momentum exchange collision frequency is independent of velocity, we have  $\mathbf{P}_c = m\mathbf{v}v_c$  and  $W_c = 0$  (or a term of order  $m/M$  in the reference frame in which the atoms are at rest). If we further neglect the effect of the ionization on the energy flux, we have the result that the right hand side of the flux equation becomes  $\mathbf{Q}_c - 5/2T\mathbf{P}_c$ . Now let us look at  $\mathbf{Q}_c$  as gotten from the Boltzmann collision integrals for stationary, infinite mass ions. It is

$$\mathbf{Q}_c = \int d^3v d\Omega \frac{1}{2} m v^2 \mathbf{v} n_a n_e \sigma(v, \Omega) (\mathbf{v}' - \mathbf{v}) \quad (7.15)$$

where as before, a primed variable denotes the velocity of an electron which ends up at velocity  $\mathbf{v}$  after a collision of angle  $\Omega$ . For particle velocities  $\mathbf{v}$  and  $\mathbf{v}'$  related by a binary collision from an infinitely massive, stationary target  $v^2 = v'^2$  since electron kinetic energy is conserved in such a collision. In the collision itself,  $\sigma(v, \Omega) d^3v = \sigma(v', \Omega) d^3v'$  by the principle of detailed balance as in Secs 3 and 4. Thus, using these relations, and the fact that  $\mathbf{v}$  is a variable of integration which can be relabeled as  $\mathbf{v}'$  in the integral, one can derive the result

$$\mathbf{Q}_c = - \int d^3v d\Omega \frac{1}{2} m v^2 (\mathbf{v} - \mathbf{v}') n_a \sigma(v, \Omega) \mathbf{v} f_e \quad (7.16)$$

Now for a scattering angle of  $\theta$ , we can write

$$\mathbf{v}' = v \mathbf{i}_v \cos \theta + v \mathbf{i}_v \times \mathbf{i}_n \sin \theta \quad (7.17)$$

where  $\mathbf{i}_n$  is a unit vector perpendicular to the plane of the collision. The perpendicular part then integrates to zero over angle, and the parallel part is related to the momentum exchange cross section. We find

$$\mathbf{Q}_c = - \int d^3v \frac{1}{2} m v^2 \mathbf{v} v_c(v) f_e \quad (7.18)$$

Expressing  $\mathbf{v}$  as  $\mathbf{u} + \mathbf{w}$ , and assuming that  $v_c$  is independent of  $\mathbf{v}$ , we find that  $\mathbf{Q}_c = -v_p \mathbf{q} + 5/2 T_e \mathbf{P}_c$ , so the equation for  $\mathbf{q}$  becomes

$$[\partial/\partial t + v_p] \mathbf{q} - (\mathbf{q} \times \Omega_c) + 5/2 (n T_e / m) \nabla T_e = 0 \quad (7.19)$$

where  $\Omega_c$  is the vector electron cyclotron frequency. Generally, for equilibrium conditions, we neglect the time dependence of  $\mathbf{q}$ . Then

the the value of  $q$  depends greatly on the magnitude and direction of the magnetic field. Specifically,

$$q_B = -5/2(nT_e/mv_p)(i_B \cdot \nabla T_e) \quad (7.20)$$

and

$$q_T = -5/2(nT_e/m)[v_c^2 + \Omega_c^2]^{-1}\{v_c \nabla_T T_e - i_B \times \nabla T_e\} \quad (7.21)$$

where the subscripts B and T mean parallel to and transverse to the magnetic field. In all cases, the temperature gradient drives the thermal conduction. If  $v_p \gg \Omega_c$ , the thermal flux is parallel to the negative temperature gradient and is proportional to the reciprocal of the collision frequency as is conventional in kinetic theory. Here however the collisions are with the atom background rather than within the species being considered. If the magnetic field is large,  $v_p \ll \Omega_c$ , the thermal flux is anisotropic in the three directions of magnetic field, temperature gradient perpendicular to the field, and cross product of the two. The thermal conduction perpendicular to the magnetic field is greatly reduced from its unmagnetized value.

## 8. Quasi-Neutrality and Sheaths in Plasmas

Far from walls, plasmas are electrostatically neutral, that is the density of electrons, (or electrons plus negative ions) is equal to the density of positive ions. This is called quasi-neutrality. At the plasma densities relevant to processing discharges, any deviation from quasi-neutrality would set up such large electrostatic fields that the electron and ion densities would rapidly equate to one another. Notice that quasi-neutrality does not mean exact neutrality; the plasma, for one reason or another may require small electrostatic fields, and these can come only from small differences in electron and ion density. As we will see, the properties of quasi-neutral plasmas are calculated using  $n_i = n_e$  as an approximate solution of Poisson's equation and then calculating the electric field from the remaining equations. Here and in the next two sections, we will give several examples of this. However quasi-neutrality only works up to a point. Near a wall or other boundary, quasi-neutrality is generally violated for one reason or another and sheaths are set up. It is these sheath regions which are so important for producing the fast ions necessary for the processing; we have seen that energetic ions are not generated in the bulk plasma.

To demonstrate the tendency of the plasma toward quasi-neutrality, we consider an infinite collisionless plasma with immobile ions and electrons with temperature  $T$ . If an added test charge is inserted in the plasma, the neutrality is violated and electrostatic potentials are set up. In terms of the electrostatic potential, the equilibrium electron density is given by Eq.(3.14). (The momentum equation for an isothermal electron fluid,  $T \nabla n = n e E$  gives the same result gives the same result.) If the perturbed potential is small compared  $T/e$ , one can linearize Poisson's equation and see that the potential decays exponentially to the ambient value with a space scale of the Debye length  $(T/4\pi n e^2)^{1/2}$ . This is an extremely small length, less than  $100\mu\text{m}$  for a plasma with density  $10^{10} \text{ cm}^{-3}$  and temperature 1 eV. This is the sheath. It is almost always small compared to any other scale length in the plasma. For instance since it is small compared to the mean free path, this sheath is generally collisionless or nearly collisionless. Thus the plasma bulk will be quasi-neutral over distances large compared to the Debye length. However there are Debye scale potential and density variations about any plasma boundary. If the plasma is time dependent, for instance from some initial deviation

from quasi-neutrality, it will then settle into a quasi-neutral state over times long compared to that for a thermal electron to cross the Debye length. That is the time for quasi-neutrality to reassert itself is about the reciprocal of a plasma period,  $(m/4\pi ne^2)^{1/2}$ . It is interesting to note that the feature scale on the workpiece (an integrated circuit for instance) can be much smaller than the Debye length. Thus once the workpiece is etched into patterns, there may be effects of charge separation in the plasma local to the pattern.

Let us consider in more detail the formation of the sheath. Consider a plasma of density  $n$  and electron temperature  $T$ , but with cold ions to be in contact with a wall. The boundary condition on the wall is that it absorbs all particles incident on it. Initially, the flux of electrons into the wall is  $n$  times the average of one component of velocity integrated over only positive velocities. This is  $n(T/2\pi m)^{1/2}$ . Thus the velocity into the wall is about the electron thermal velocity, and the electrons within a Debye length of the wall are cleared out within about a plasma period. The wall charges up negative and begins to accelerate the ions toward the wall. Thus there is a flux of particles toward the wall, and this flux is assumed to be absorbed. The question then is under what conditions a steady state sheath can be generated and what the particle flux and electric current to the wall is.

Since the sheath has Debye length scale, which is assumed to be much smaller than mean free path or geometric scale length, a one dimensional model is valid. The sheath is at the right hand edge of a collisionless plasma. The electrons have temperature  $T$  and the ions are cold. Both have number density  $n_0$  far from the sheath where the potential is defined to be zero. Since quasi-neutrality is violated in the sheath, it is described by Poisson's Equation

$$d^2\phi/dx^2 = -4\pi e(n_i - n_e) \quad (8.1)$$

To solve this, we need the electron and ion density in terms of  $\phi$ . The electron density we have derived already,  $n_e = n_0 \exp e\phi/T$ . The ions are described in terms of a flux toward the sheath. At  $x=-\infty$ , the ion velocity is  $u_0$ . Since  $nu = n_0 u_0$ , the ion density in terms of the potential is  $n_i = n_0 u_0 / [u_0^2 - 2e\phi/M]^{1/2}$ .

We expect the ions to accelerate through the sheath, so we expect  $\phi < 0$ , that is we expect the plasma to have a higher positive

potential than the bounding surfaces in contact with it. Also, we expect the sheath to have higher ion density than electron density, since the whole idea is that the ions are following the electrons out. For small  $\phi$  the electron and ion densities follow by linearization,  $n_i = n_0(1 + e\phi/Mu_0^2)$  and  $n_e = n_0(1 + e\phi/T)$ . For  $\phi < 0$ , the ion density in the sheath is greater than the electron density only if  $Mu_0^2 > T$ . Also from Eq.(8.1) it is clear that if this is so, the sheath is exponentially decaying into the plasma, otherwise Eq.(8.1) has a solution which is oscillatory in  $x$  and the solution does not have the character of a sheath, but rather of a wave. Thus in order for a sheath to be formed, we must have

$$u_0 > [T/M]^{1/2} \quad (8.2)$$

For the case of an equality in Eq.(8.2), this is called the Bohm criterion<sup>48</sup>. The Bohm criterion is often used as a condition separating the plasma from the sheath, and in general this is correct. However the situation is complicated in general, and to determine the actual condition, one must look at the fluid solution both near and far from the wall. The case we have been considering, a semi-infinite one dimensional collisionless plasma in contact with a wall is underspecified. To satisfy the sheath condition, any incident ion velocity greater than  $\sqrt{T/M}$  will suffice and smaller velocities will not.

To come up with a simple specified system, we will consider a spherical instead of planar wall. We will assume that the spherical radius is small compared to any other physical size characterizing the plasma, but large compared to the Debye length. Thus there is an outer quasi-neutral region of size characteristic of the radius, and a Debye length scale inner region, right near the sphere which is nearly planar. The boundary condition on the sphere is that it absorbs every charged particle impinging on it and does not emit or reflect anything. Far from the sphere, the outer region is assumed to be an infinite homogeneous plasma with cold ions, electrons of temperature  $T$ , and number density  $n_0$ . Thus there is both a particle flux and an electric current to the sphere, and we wish to relate these to the potential of the sphere. The potential of the plasma far from the sphere is zero, and this is defined as the plasma potential.

Using the relation between the potential (and electric field) and electron density, we find that the steady state ion momentum equation becomes

$$M u \frac{du}{dr} = -(T/n) \frac{dn}{dr} \quad (8.3)$$

where we have assumed quasi-neutrality,  $n_e = n_i = n$ . The steady state mass conservation equation, in spherical geometry becomes

$$\frac{d}{dr}(r^2 n u) = 0 \quad (8.4)$$

Combining these, we find a single equation for  $u$ ,

$$\frac{du}{dr} = -2u/r [1 - M u^2/T] \quad (8.5)$$

Notice that this equation is singular at  $u^2 = T/M$ , the precise velocity defined by the Bohm criterion. However the singularity is only a singularity of the slope,  $u$  itself is defined by Eq.(8.5) right up to the singularity. In fact the equation can be integrated analytically. To specify the outer solution, we need only integrate it subject to the appropriate boundary condition.

The appropriate boundary condition for the outer solution is that the singularity is at  $r=r_0$ , the surface of the sphere. To see this, note that at the singularity, the infinite slope means that quasi-neutrality has broken down and that Poisson's equation must be used instead of the quasi-neutrality condition. However Poisson's equation has no singularity, but it has a higher derivative,  $d^2\phi/dx^2$ , which introduces a much smaller length scale where it is needed. Thus the singularity is really the mathematical treatment begging for inclusion of the shorter length scale, or higher derivative. Since the Debye length is assumed to be much less than the radius of the sphere, on the scale length of the outer solution, the singularity is at the spherical surface (or actually a few Debye lengths away). The outer solution, determined by integrating Eq.(8.5), subject to the boundary condition that the  $u = \sqrt{T/M}$  at  $r=r_0$  is

$$r^2 u \exp[-M u^2/2T] = r_0^2 (\sqrt{T/M}) \exp -1/2 \quad (8.6)$$

This solution is also consistent with the boundary condition at  $r=\infty$ ,  $u=\phi=0$ . At the singular point, the electrostatic potential is given by

$e\phi/T = -1/2$ , so the density is given by  $n=n_0\exp-1/2$ . Thus the mass flux into the sphere is

$$dM/dt = 4\pi r_0^2 n_0 M(\sqrt{T/M})\exp-1/2 \quad (8.7)$$

and it is specified entirely by the outer solution.

The singular point near the spherical surface marks the beginning of the inner solution. To actually determine the total solution, one must in general do a matching of the inner and outer solutions. Typically this is complicated and involves intermediate solutions with scale lengths that are some fractional power of products of the scale length of the inner and outer solution. In many cases the information desired depends in detail on this matching. The most famous case in the plasma physics literature is a tearing mode, where the growth rate depends on precisely how the inner and outer solutions are matched<sup>52,53</sup>. Just patching them together at the singularity will not give the growth rate of the mode.

Fortunately, the case we are discussing here is much simpler, and the main information required, the current as a function of sphere Voltage can be obtained with a simple patch. We are not here interested in the precise structure of the transition region for its own sake, so we will not look into the more complicated problem of the detailed matching. However other sheath problems in processing discharges may require this procedure.

The equation for the nonneutral sheath region is Poisson's Equation

$$d^2\phi/dx^2 = -4\pi en_0[(-T/2e\phi)^{1/2}\exp-1/2 - \exp(e\phi/T)] \quad (8.8)$$

where we have assumed as initial values, the parameters at the outer singular point. If this equation is initialized with  $e\phi=-T/2$  and a small negative slope, a sheath solution with a Debye length scale will result. Since the sphere is assumed to simply absorb all incident particles, and since the electron density is known as a function of  $\phi$ , we can calculate the current as a function of the sphere Voltage  $\phi_0$ . Of course the ion current to the sphere is simply  $e/M$  times the ion mass accumulation. The electron current density is that from half a Maxwellian at the electron density of the wall. Thus the current is

$$I = -4\pi\epsilon_0^2 n_0 [(T/2\pi m)^{1/2} \exp(e\phi_0/T) - (\sqrt{T/M}) \exp(-1/2)] \quad (8.9)$$

For this solution to be meaningful, the potential of the sphere must be less than  $-T/2e$ , or the outer solution will be non singular. At this potential, the current to the sphere is large and negative, it is nearly the full electron current of a half Maxwellian electron distribution. As the potential is lowered, the magnitude current decreases until it vanishes at a potential  $\phi_f$

$$e\phi_f/T = 0.5[\ln(m/M) - 1] \quad (8.10)$$

This is called the floating potential and is the potential a small foreign body will float to if it is inserted into the plasma, but cannot draw current. For potentials much below this virtually all of the electron current is cut off, and the current to the sphere is positive current from the ion flux, independent of the inner solution.

Thus for the case of the absorbing sphere, the Bohm criterion is correct, but the justification lies in the singular nature of the outer solution. In fact the inclusion of ion inertia will nearly always generate a fluid singularity where the flow speed is equal to the sound speed. It is this singularity which marks the edge of the outer region and therefore the place where quasi-neutrality breaks down and Poisson's equation must be used to describe the plasma. The singular nature of the outer solution, at just the Bohm velocity, is then what usually justifies Bohm criterion. While this singular point is the justification, in many cases the singularity can be approximated away as we will see in the next section.

We next consider what happens when the Voltage on the sphere or workpiece is lowered still further. If the magnitude of the Voltage is much greater than the electron temperature, electrons are virtually excluded from these regions of the sheath according to Eq.(3.14). For instance the electron temperature might be 1 eV, and the negative Voltage on the workpiece might be a kilovolt. In this case, electrons will be excluded from perhaps 99% of the Voltage drop. The edge of the electron region will be the source of nonneutral ion flux, and the current will be purely ion current from the edge of the electron boundary to the workpiece. Since the ion current emerges from the sheath region at low Voltage, the ion region is a planar ion diode. Across this ion diode, the relation

between Voltage, current and thickness  $s$  is given by the Child-Langmuir space charge limited current equation

$$J(\text{A/cm}) = 10^{-8} (M_a/M)^{1/2} V^{3/2} (\text{volts}) / s^2 (\text{cm}) \quad (8.11)$$

where  $M_a$  is the mass of an argon atom. For instance for a kilovolt across a centimeter in an argon plasma, the ion current is about  $3 \times 10^{-4} \text{A/cm}^2$ . Thus the ion diode thickness is generally much greater than the Debye length which characterizes the electron-ion sheath we have just discussed. However to simplify the analysis, we have assumed that the ion sheath thickness is small enough that the ions can be regarded as collisionless. The extensions of the Childs-Langmuir law to the case of collisional ions are straightforward, and one case will be worked out as it becomes necessary in the next section.

One difficulty is that in a plasma, the Voltage and current are not simultaneously specified; only one is given, and the other is derived from the Ohm's law for the plasma or its equivalent. Thus one additional relation is required to determine the ion sheath parameters. In the next sections we will see how this determination can be made for DC and RF discharges.

For now, we will consider the simpler case of plasma immersed ion implantation (PIII). In this case a workpiece is inserted in the plasma of number density  $n_0$ , and is pulsed with a large negative Voltage, a Voltage we will assume to be much greater than  $T/e$ . Before the Voltage is turned on, the workpiece will be bombarded with a low energy ion flux as we have just described. Then at time  $t=0$ , a Voltage pulse  $V(t)$  is imposed. Then the plasma electrons begin to be excluded from a region of width  $s$  near the workpiece. At  $t=0$ ,  $s=0$ . We will assume that  $s$  is changing with time very slowly compared to the ion flight time across the sheath region. Then the sheath behaves instantaneously like an ion diode. However the current density is simply the rate that the sheath eats its way into the plasma. That is

$$-J = n_0 e ds/dt \quad (8.12)$$

where for the configuration we envision, the plasma on the left of the workpiece, so  $J > 0$  and  $ds/dt < 0$ . Equating the current to the ion diode result, we find a single equation for  $s$  (now interpreted as the magnitude of the sheath width) in terms of the Voltage pulse

$$ds/dt = 6 \times 10^{12} (M_a/M)^{1/2} V^{3/2}(t) / n_0 s^2 \quad (8.13)$$

where  $n_0$  is in  $\text{cm}^{-3}$ . Integrating once, we have

$$(1/3)s^3 = 6 \times 10^{12} (M_a/M)^{1/2} \int_0^t V(t) dt / n_0 \quad (8.14)$$

If the Voltage turns on abruptly in time, the nature of the solution of Eq.(8.14) is that at early time  $s$  changes rapidly in time so that the assumption of a stationary ion sheath is invalid. In the more likely case of an adiabatic rise to the final Voltage, Equation (8.14) should be a good description of the ion diode width as a function of time. From this and the Voltage pulse shape, one can calculate the current pulse and therefore the charge dose as a function of energy which is embedded in the workpiece.

So far we have considered only the flux of energetic charged particles to the workpiece, those generated in the sheath. However in processing discharges, there are also energetic neutrals impinging on the workpiece. The only apparent source of these neutrals is ion charge exchange collisions in the sheath. That is an ion, in colliding with a neutral, takes an electron from the neutral. The ion then becomes a fast neutral and the neutral becomes a slow ion. Charge exchange collisions are often the most important of the ion-neutral collision processes. If we assume that the collision rate is small enough that ion collisions are a small perturbation on the overall ion flux through the sheath, one can calculate the flux of fast neutrals from the charge exchange cross section  $\sigma_{ex}(E)$  where  $E$  is the ion energy. If the ion density and velocity at a position  $x$  in the sheath are  $n_i(x)$  and  $v(x)$ , then the flux of neutrals  $dF$ , produced in region  $dx$  of the sheath is given by

$$dF = n_i(x)v(x)n_a\sigma(E)dx \quad (8.15)$$

where  $n_a$  is the atom number density. The relation between ion energy (or velocity) and position in the sheath completes the description. Thus from a knowledge of the charge exchange cross section and sheath parameters, one can calculate the flux of energetic neutrals onto the workpiece for the case where it is a small perturbation of the ion flux.

## 9. DC Discharges in Cylindrical and Planar Geometry

As we have seen in the previous section, a steady state discharge in contact with a wall is characterized by a large region which is quasi-neutral, which then transitions, near the wall, to a sheath region which is nonneutral. Generally the quasi-neutral part of the plasma is described by fluid equations and in general, two and three dimensional effects can be very important, although the simplest one dimensional treatments are often useful. The sheath region is usually thin compared to macroscopic scale lengths, and perhaps even to mean free paths. It is usually one dimensional. However a fluid theory typically does not provide a full description of the sheath. For instance as we have seen in the last section, the electron boundary condition for an absorbing wall came directly from the knowledge of the distribution function (the particle flux for a half Maxwellian), and not from a calculation of fluid properties. This is the general approach that we will use to calculate the properties of processing discharges.

We will start with a description of discharges in cylindrical geometry. One experimental fact is that the positive column of a glow discharge can be arbitrarily extended in length with no change of its properties. Chapman quotes Brown and Hittorf regarding the latter's attempt to measure a fundamental length of the positive column. He extended the length all around the lab until "a frightened cat pursued by a pack of dogs came flying through the window. 'Until an unfortunate accident terminated my experiment, the positive column appeared to extend without limit'" Hittorf reported. Thus an infinite cylindrical model of the discharge is in accord with observations.

Let us assume that the steady state cylindrical plasma is produced by a dc current. We assume that there is a central part, containing virtually all of the plasma volume which is quasi-neutral. Also we will neglect electron inertia and ion inertia in the axial and azimuthal direction. Near the wall, the radial ion inertia is important in that it is responsible for the singular behavior, so we will start by including it, and then show how the problem can be simplified by approximating it away. The quasi-neutral region is described by the number density equation for electrons, the momentum equation for electrons and ions, and the energy equation for electrons. As far as the ion energy goes, we account only for the ionization energy which the ions are defined as having. Furthermore,

we assume the presence of an axial magnetic field throughout the discharge.

We start with the momentum equation in the z direction

$$-eE_z = m u_{ez} \nu_e \quad (9.1)$$

where  $\nu_e$  is the electron momentum exchange collision frequency assumed to depend linearly on gas density, but otherwise is a constant. In steady state,  $\text{curl } \mathbf{E} = 0$ , so that in the plasma,  $E_z$  is constant and cannot have any radial variation. For virtually all gases,  $m \nu_e \gg M \nu_i$ , so that the axial current is carried by electrons and the energy input from the external circuit goes nearly entirely into the electrons. From Eq.(9.1), one can easily calculate the current density and total current

$$I = e^2 E_z / m \nu_e \int d^2 r n(r) \quad (9.2)$$

The total power input into the electron thermal energy, from Eq.(7.5) is  $n m \nu_e u_{ez}^2$  where  $u_e$  can be related to the electric field or total current through Eqs.(9.1 and 9.2). We assume that  $u_{ez}$  is much greater than the radial outward flux of electrons and ions so that energy input or output arising from the radial motion is small. Generally we regard the total current as the specified quantity. In terms of it, the power input per unit length is

$$dP/dz = m I^2 \nu_e / e^2 \int n(r) d^2 r \quad (9.3)$$

This then describes the Ohms law and energy input to the plasma. We now consider the radial particle and energy flux, starting with the particle flux. We neglect all inertia except radial ion inertia, which is responsible for the singular nature of the quasi-neutral solution. Then the steady state density and momentum equations become

$$(1/r) d/dr (r n u_r) = \alpha_i n N \quad (9.4)$$

$$M u_r du_r/dr = e(E_r + u_{i\theta} B/c) - M u_r \nu_i \quad (9.5)$$

$$0 = -e u_r B/c - M u_{i\theta} \nu_i \quad (9.6)$$

$$0 = -e(E_r + u_{e\theta}B/c) - mv_e u_r - (1/n)d/dr(nT) \quad (9.7)$$

$$0 = eu_r B/c - mu_{e\theta} v_e \quad (9.8)$$

where  $N$  is the neutral density and the right hand side of Eq.(9.4) is the ionization rate., where  $\alpha_i$  depends strongly on electron temperature as discussed in the section on impact ionization. The  $v$ 's also depend linearly in  $N$ , but this dependence is not explicitly shown. Also  $T$  is the electron temperature, the only significant temperature in our discussion. The ions are assumed cold both because very little of the Ohmic power goes into them, and also because they equilibrate rapidly with the much denser neutral gas component.

Equations (9.5-9.8) can be reduced to the single equation for  $u_r$  and  $n$

$$Mu_r du_r/dr = -\{A_e + A_i\}u_r - (1/n)d/dr(nT) \quad (9.9)$$

Here,

$$A_e = mv_e[1 + \Omega_e^2/v_e] \quad (9.10)$$

with an analogous expression for  $A_i$ , where  $\Omega$  is the appropriate cyclotron frequency. This and Eq. (9.4) for  $n$  are two of the equations for the density, radial velocity and temperature. By solving individually for the density and velocity derivative, one can determine that the solution becomes singular, in that the derivatives approach infinity, when the radial velocity is the ion sound speed.

Let us now discuss a way in which an approximate solution can be obtained without involving the detailed singular structure of the quasi-neutral solution. Neglecting ion inertia, we see that the ion radial velocity is given by

$$u_r = -[n(A_e + A_i)]^{-1} d/dr(nT) \quad (9.11)$$

Notice that the velocity is determined by the magnetic field as well as collisionality of both species. For an unmagnetized plasma typically  $A_e \ll A_i$  so the radial velocity controlled by the ions. However it does not take a large magnetic field to increase  $A_e$  until,

it is larger than  $A_i$ , thereby making the electrons the dominant species in controlling the drift radial velocity. At the center of the plasma where radial derivatives are zero, the velocity is zero. However as one approaches the edge, where the density is less, the velocity increases both because the derivatives increase, and also because the  $n$  in the denominator decreases. As some point, this expression velocity will equal the ion sound speed. This then will be defined as the edge of the quasi-neutral region. Typically this will be at a density much below the central density and we will characterize this density by  $n_s$ . Its actual value, in terms of the the central density  $n_0$ , will depend on the nature of the outer solution.

The equation for the density then becomes

$$(1/r)d/dr\{r[A_e+A_i]^{-1}d/dr(nT)\} = -\alpha_i(T)Nn \quad (9.12)$$

This must satisfy the boundary condition that  $n=n_s=0$  at the plasma edge. For given temperature profile, Eq.(9.12) is a linear equation for  $n$ , so that it does not specify the magnitude of the density, but only specifies the relative density profile as well as an eigenvalue insuring the boundary conditions are satisfied at both the center and edge. Approximating the temperature as constant, we find that

$$n(r) = n_0 J_0(\kappa r) \quad (9.13)$$

where

$$\kappa^2 = \alpha_i(T)[A_e+A_i]/T \quad (9.14)$$

At the plasma wall  $r=a$ , the eigenvalue is determined approximately by  $\kappa a=2.4$ , the first zero of the Bessel function. Thus we have determined the relative density profile and the temperature. Notice that for a low temperature plasma,  $\alpha_i$  is a very rapidly varying function of  $T$ . Thus large changes in things like wall radius will have only as small effect on the temperature. It is particularly interesting that the magnetic field has little effect on the plasma solution as well. Although the particle flux may be greatly reduced, this is compensated for in steady state, by a relatively small reduction of the plasma temperature. However, since the plasma has finite length, the particle loss to the ends of the system along the field lines may dominate the losses in an actual magnetized plasma. We will discuss this configuration shortly.

Thus we have many characteristics of the quasi-neutral solution. At the singular point, the quasi-neutral solution joins smoothly to sheath region as discussed in the previous section. Since the wall is assumed to draw no current, the wall is at the floating potential, which was also solved for in the previous section in terms of the potential at the sheath edge as obtained from the quasi-neutral solution. The sheath solution in the previous section was derived for the case of an unmagnetized plasma. Here we will show that as long as  $\omega_{pe} \gg \Omega_e$ , (the usual condition in processing plasmas) the sheath is unaffected by the magnetic field.

The sheath is assumed to be collisionless, so that here, magnetic deflection of electrons must be balanced by electron inertia. Solving the electron momentum equation in the  $y$  direction (corresponding to the  $\theta$  direction in the cylindrical configuration) and substituting in  $x$ , we find that the electron momentum equation is integrable, and integrates to

$$1/2 m(u_{ex}^2 - u_{exs}^2) = -1/2 m \Omega_e^2 (x - x_s)^2 + e(\phi - \phi_s) - T \ln(n/n_s) \quad (9.15)$$

where a subscript  $s$  denotes a quantity at the sheath edge. Since the sheath velocity is typically  $\sqrt{T/M}$ , the left hand side can be neglected. If the sheath width is of order  $\lambda_{de}$ , the size of the magnetic field term is of order  $(\Omega_e/\omega_{pe})^2$  as compared to the other terms, so it too can be neglected. Thus for sufficiently weak magnetic fields, the relation between density and electrostatic potential is as in the unmagnetized case. Since the ion Larmor radius at the sound speed is very large compared to the electron Debye length, the ions are also unmagnetized in the sheath. Thus the sheath solution is as in the unmagnetized case as long as  $(\Omega_e/\omega_{pe})^2 \ll 1$ .

Now we will calculate the density by considering the one remaining relation not yet considered, the energy conservation relation. The energy input to the plasma per unit length is given by Eq.(9.3). The energy losses are either through charged particles or through other channels. We will consider first the charged particle channel. Every charged particle flows out of the plasma and takes its energy with it. As before, the wall is assumed to be a perfect absorber of charged particles. With the ion flux goes the ionization energy and the ion kinetic energy that it has when it strikes the

wall. The ion mass flux into the sheath is given by  $n_s \sqrt{T/M}$ . Thus the ionization energy convected out is  $E_i n_s \sqrt{T/M}$ . As the ion convects through out the sheath, it falls through a potential corresponding to the difference between the floating potential and the potential at the sheath edge given in Eq.(8.10). Thus the ion energy flux convected out is  $(n_s \sqrt{T/M})(T/2)[1 + \ln(M/m)]$ . Next we consider the electron energy flux out of the plasma. The electron distribution is in contact with the wall, so that the electron energy flux out is the electron energy flux of half a Maxwellian, analogous to the issue of electron density flux. This calculation gives the result that the energy flux is  $2nT(T/2\pi m)^{1/2}$ . As we have derived in the previous section, the electron density at the floating potential is  $(m/M)^{1/2}$  times the density at the sheath edge. Thus the surface power convected out per unit length is

$$\begin{aligned} dP_s/dz = & 2\pi r n_s (T/M)^{1/2} [E_i + (T/2)(1 + \ln(M/m)) \\ & + 2T(T/2\pi M)^{1/2}] \end{aligned} \quad (9.16)$$

In addition to the surface flux out, there is a volumetric power loss from radiation as well as from heating the neutral gas. This volumetric power loss is

$$dP_v/dz = \int d^2r (3m/M) v_e n T + \int d^2r n P_r \quad (9.17)$$

where  $P_r$  is the radiated power loss per electron. Note that the volume power loss is proportional to  $N$  while the surface power loss is not. However the total power loss is proportional to the electron density; to the density at the singular surface for the surface loss; and to the average density for the volume loss. These two are related to each other through the density profile; the Bessel function in our case. The power input per unit length is given by Eq.(9.3). Notice that this is proportional to the reciprocal of the average density. Equating the power in to the power out gives us an expression for the overall electron and ion density of the plasma. We find that the electron density is proportional to the total current  $I$ .

Let us now recall the molecular oxygen plasma discussed in Section 5. For the low density plasma, it was pointed out that there was no sensible equilibrium. For instance for the  $O_2$  species, there were only loss terms, while for electrons there were only

production terms. For O there is only a single, relatively weak loss mechanism fighting many much stronger production mechanisms, considering that O<sub>2</sub> is assumed to be the major species. An equilibrium density for O<sub>2</sub><sup>+</sup> was possible, but at much too high a value. We see now that the other part of the issue is the electrodynamics of the plasma itself. The loss of electrons as well as positive ions to the walls now allows equilibria to form as we have just calculated here. As far as the O<sub>2</sub> is concerned, from low density chemistry alone, there were only loss terms. However as the O<sub>2</sub><sup>+</sup>, O<sup>+</sup>, O and the associated electrons reach the walls of the discharge, they recombine. That is for an electron and ion to recombine, there must be a third body present to take up the energy and momentum. The wall serves as a third body here. We have assumed for a boundary condition that the wall absorbs all particles impinging upon it. However once these particles are absorbed, it is likely that, for a totally inert wall, they recombine to the energetically favored species, O<sub>2</sub> in this case. Thus the wall is a source of O<sub>2</sub> which allows an equilibrium to form regarding this species as well. Thus as far as the O<sub>2</sub> is concerned, there are volumetric losses, which are balanced by production at the surface and inward particle flux.

For neutral atomic oxygen the reverse is the case, there are volumetric production mechanisms leading to a steady state flux to the walls where it recombines to form O<sub>2</sub>. Thus the steady state number density equations for O<sub>2</sub> and O are

$$(1/r)d/dr(rF_a) = S_a \quad (9.18)$$

$$(1/r)d/dr(rF_b) = S_b \quad (9.19)$$

where we have used the notation of Section 5 where a corresponds to O<sub>2</sub> and b corresponds to O, and F is a number density flux and S is a source. For O<sub>2</sub>, S<sub>a</sub> is negative, the flux is inward, and just balances the volumetric loss. If O<sub>2</sub> is the predominant species, then F<sub>a</sub> = au<sub>a</sub> where a is the equilibrium density. Thus the velocity as well as the flux can be obtained. For O the opposite is true, and there is an outward flux to the wall. This atomic oxygen is of course the free radical and often the plasma is used simply to produce it so that it can react with the wall material and chemically affect it. In fact more realistic models of the processing discharge would have to account for the reactions at the wall and not simply assume that everything just recombines to form the initial products. Hence to

summarize, the equilibrium properties of low density processing discharges, and the associated fluxes of the free radicals to the wall or workpiece, are not determined by chemistry alone, but by a combination of it as well as plasma electrodynamics and reactions at the wall.

We now consider the case of a planar discharge, and in doing so, will concentrate mostly on the differences between it and the cylindrical case. There are two principal differences. First is the fact that the velocity of both species is entirely in the  $x$  direction, so that this single velocity component describes both the electric current and the particle flux to the walls. Second is the fact that there is a cathode sheath (usually called the cathode fall), which we will see is a very different sort of sheath from what we have described up to now. The cathode fall is much more complicated and our description of it will be more qualitative than quantitative, but will identify the principal mechanisms responsible for its formation.

In a one dimensional configuration carrying current density  $J$ , the electron and ion velocities are related by

$$u_e = u_i - J/ne \quad (9.20)$$

As before, we assume that the main part of the plasma is quasi-neutral, with number density and momentum equations

$$d/dx(nu_i) = \alpha_i n N \quad (9.21)$$

$$0 = -d/dx(nT) - neE - nmv_e(u_i - J/ne) \quad (9.22)$$

$$0 = neE - nMv_i u_i \quad (9.23)$$

Unlike the cylindrical plasma, here the electric field does have variation in  $x$ , whereas the current density  $J$  does not. Eliminating the electric field, we find a single equation for density (approximating  $T$  as constant and  $Mv_i \gg mv_e$  as before)

$$d/dx[-(T/Mv_i)dn/dx] = \alpha_i n N \quad (9.24)$$

and the ion and electron velocities are

$$u_i = -(T/nMv_i)dn/dx + (mv_e/(mv_e+Mv_i))J/ne \quad (9.25)$$

$$u_e = -(T/nMv_i)dn/dx - (Mv_i/(mv_e+Mv_i))J/ne \quad (9.26)$$

Thus both the electrons and ions have a gradient driven component of velocity and a current driven part. The gradient parts are the same, while the electron current driven part is much greater than the ion current driven part. Thus the result is quite analogous to the cylindrical case, except that both parts of the velocity are in the same direction here.

The electron density profile and temperature can be determined from Eq.(9.24) analogous to the case of Eq.(9.12) for the cylindrical plasma. Now let us consider the boundaries at the electrodes. As before, our assumption is that the boundaries absorb all incident charged particles. The anode boundary condition is relatively straightforward. There is an electron and ion flow into the anode, and its potential is determined so that the current density is just  $J$ . This is analogous to the calculation for the cylinder wall except that now the potential is somewhat higher than the floating potential because the anode draws a net electron current. In terms of  $J$  one calculates the anode potential relative to the sheath edge and from that, the various energy fluxes. The sheath width is several Debye lengths.

Now let us consider the cathode. By the assumed boundary condition, the cathode does not emit particles, so the only way it can draw the appropriate current is if a flux of ions is absorbed there. However there is an immediate problem with this scenario, if one assumes the same type of sheath as on the anode or cylindrical wall. As the potential is lowered, electrons are all excluded and ultimately the cathode will draw the ion saturation current  $n_s e \sqrt{T/M}$ . The problem is that the discharge current is considerably greater than the ion saturation current in almost all cases. One might think that the solution is simply to lower the cathode potential further, but this is not the solution. Lowering the cathode potential will accelerate the ions to higher energy, but will not increase their current. In steady state the current density is constant no matter what the Voltage drop.

The solution is a very different type of cathode sheath, and a much more complicated one. An accurate description can most likely

come best from a particle simulation, but we will derive the qualitative features here. The only way that the cathode sheath can draw a current larger than the ion saturation current is if electron current is converted to ion current there. This can only occur collisionally through the ionization term in the steady state electron and ion density equation. Thus the cathode sheath is inherently collisional, and therefore is of much greater length than the anode or wall sheath.

We will model the configuration as having the wall on the right, so ion velocity into the wall is positive and  $E > 0$ . Any electron velocity in the sheath is in the negative direction (meaning positive electron current). The equations for the electric field and currents are Poisson's equation and the continuity equations for electron and ions. They are

$$dE/dx = 4\pi e[(j_i/u_i) + (j_e/u_e)] \quad (9.27)$$

$$dj_i/dx = -\alpha_i N j_e/u_e \quad (9.28)$$

$$dj_e/dx = \alpha_i N j_e/u_e \quad (9.29)$$

Notice that the continuity equations now allow the exchange of electron current for ion current while conserving total current density,  $j = j_e + j_i = \text{constant}$ . However this exchange takes place over a collisional (actually ionization) scale length. Over the collisional scale length  $u_e = -eE/mv_e$  and  $u_i = eE/Mv_i$ .

We will now briefly discuss two aspects of the solution of Eq.(9.27-9.29) before developing the solution. First of all, up to now, we have specified boundary conditions of walls that absorb particles but do not emit them. Actually, for the cathode sheath, the boundary is a little more complicated in that whenever an energetic ion hits the wall, it typically knocks out an electron with some probability  $\gamma$ . For most materials and for most ion energies,  $\gamma$  is between about 0.1 and 0.2. We will see that our solution for the cathode sheath depends weakly on this  $\gamma$  value. Secondly, the sheath fields are high, and the electrons and ions are accelerated to large velocity, much larger velocity than what they obtain in the fields of the bulk plasma. Thus it is not at all certain that drift velocities will be much smaller than thermal velocities, or even that a fluid treatment will be strictly valid. The resistive heating

on the electron and ion plasmas in the sheath are much greater than what they are in the bulk, so we expect temperatures to be much higher, as is generally observed. The cathode sheath, or cathode fall as it is called, is generally the brightest portion of a glow discharge. Thus, although it is approximate, we will consider  $\alpha_i$  to be strictly a constant.

To solve Eqs.(9.27-9.29), first express  $j_e$  as  $j-j_i$  in Eq.(9.27). Then divide Eq.(9.27) by Eq.(9.28) to obtain a single equation relating  $E$  to  $j_i$ . Assuming that  $j_i=0$  at the edge of the sheath where  $E=0$ , we find

$$E = (4\pi M v_i / \alpha_i N m v_e) [-j_i - j \ln(1 - j_i/j)] \quad (9.30)$$

At the cathode, where  $j_i = j/(1+\gamma)$ , we find

$$E \approx 4\pi M v_i j / \alpha_i N m v_e \quad (9.31)$$

for the values of  $\gamma$  in the range specified. This in turn specifies the energy of the impinging ions. The energy flux of ions into the cathode is given  $E_i$  plus this energy times the ion particle flux. This ion energy flux in turn is one of the power loss mechanisms, which plays a role in determining the overall electron density.

To solve approximately for the spatial structure of the sheath, we will approximate the solution for  $E$  in terms of  $j_i$  by expanding the natural log. We find

$$E \approx 2\pi M v_i j_i^2 / \alpha_i m v_e j \quad (9.32)$$

Then we assume that the charge density in the sheath is dominated by the ion density; for electron current equal to or less than the ion current, the electron density is much less because the electron flow speed is much greater. Then expressing  $j_i$  and  $u_e$  in terms of  $E$ , we find a single equation for  $E$  which can be integrated analytically. We find that the sheath width is given by

$$L = (4\pi\sqrt{2/3}) M v_i j_e / (m v_e)^2 \alpha^2 N^2 \quad (9.33)$$

and the Voltage drop across the sheath is given by

$$V = (16\pi\sqrt{2/3} m v_e) (M v_i / m v_e)^2 j_e^2 / (\alpha N)^3 \quad (9.34)$$

Typically, unless the discharge is very long, the Voltage drop across the sheath is the dominant Voltage drop in the plasma. If this is so, and the discharge circuit is constant Voltage, then the current is proportional to neutral pressure squared, as specified by Eq.(9.34). Thus we see that the cathode sheath is very different from other sheaths, and is dominated by collisional exchange of electron and ion current through the ionization. The relatively large fields and the collisionality of the plasma there gives rise to more heating and higher plasma temperature than what one finds in the bulk. To better quantify the sheath, the electron temperature would have to be calculated, with the energy equation, or perhaps better still, with a particle simulation since this portion of the plasma is probably not really fluid like.

## 10. RF Discharges in Planar Geometry

In processing discharges, power at an rf frequency  $2\pi\omega$ , typically 13 Mhz, is often used instead of dc power. As we will see, this allows for high ion fluxes at both sheaths. For the dc discharge, the cathode sheath was inherently collisional. In the case of the rf plasma, the sheath may be collisionless, and it is the presence of the oscillating current allows this. The fact that the sheath can be collisionless would appear to allow for rf discharges at neutral pressures less than the minimum required for dc discharges. However sheath lengths are long compared to the Debye length, so that while collisionless sheaths are allowed, collisions in the sheath are usually important too. However to simplify the analysis, we consider only collisionless sheaths here. Furthermore, the workpieces typically do not have to be conductors, because there is not necessarily any dc current drawn. Near the workpiece, the rf electric current is displacement rather than conduction current.

To model the rf discharges in planar geometry, we assume that in the central, quasi-neutral region, each fluid quantity has an average value, and a value oscillating at the rf drive frequency. The idea then is to write the fluid equations as two separate sets of fluid equations, one for the dc quantities, and one for the quantities oscillating at frequency  $\omega$ . Since the equations are nonlinear, there will be coupling from one set to the other.

We denote the rf quantities with an underline, and generally we assume that these are small compared to the dc quantities, so that a perturbation theory can be applied. We will make the same simplification that we did with the dc discharges, namely we will assume in the mass and momentum equation that the temperature is constant. Furthermore, since quasi-neutrality establishes itself in times of order the inverse plasma period ( $\ll \omega^{-1}$ ) and over distances of order the Debye length, both the dc and rf plasma will be assumed to be quasi-neutral. This central quasi-neutral region then attaches itself to a sheath near the boundary. This sheath is not neutral, and furthermore, the separation of the rf and dc components becomes rather complicated. As in the dc plasma, the currents as well as mass and energy losses of the sheath specify the boundary condition for the central plasma region.

The rf momentum equation for the the central quasi-neutral part then becomes

$$m \partial \underline{u}_e / \partial t = e \underline{E} - m v_e \underline{u}_e \quad (10.1)$$

In writing Eq.(10.1), we have assumed that there is no dc current, meaning that  $\underline{u}_e$  is equal to  $\underline{u}_i$  and is just the ambipolar diffusion velocity of electrons and ions. This velocity is assumed to be small and negligible on the left hand side of Eq.(10.1). We have also used the fact that  $\underline{n}_e = 0$  due to quasi-neutrality and the fact that  $\underline{n}_i = 0$ , and have also used our simplification  $\underline{I} = 0$  in the momentum equation. This gives

$$\underline{u}_e = e \underline{E} / m(-i\omega + v_e) = -\underline{J} / ne \quad (10.2)$$

which is also the Ohm's law for the plasma. In applying Ohm's law, it is necessary to keep in mind that  $\underline{J}$  has no  $x$  dependence due to quasi-neutrality, while the  $x$  dependence of  $\underline{E}$  is as specified by Eq.(10.2), that is for constant  $v_e$ ,  $\underline{E}$  is proportional to the reciprocal of the density, just as in the case of the planar dc discharge.

Now let us consider the dc component of the electron momentum equation. Neglecting electron inertia for the dc part,

$$0 = -eE - m v_e v_e - n^{-1} T dn/dx \quad (10.3)$$

That is with the approximations we have made regarding electron inertia, quasi-neutrality and rf temperature, there are no coupling terms from the rf equations to the electron momentum equation and the momentum equations are the same in the rf and dc plasma. These are solved as in the case of the dc planar plasma. The boundary condition is that the wall is at the singular point, or if the ion inertia is approximated away, then the wall is taken at the position where the outward velocity is the ion sound speed. This defines the position where the quasi neutral part matches onto the sheath. As in the dc case, the relative density profile and electron temperature are determined. The overall density is determined by the energy balance.

We now turn to the dc electron temperature equation. There is a power input from the Ohmic heating. If  $\underline{J} = -J_0 \sin \omega t$  then the average power input in the electron temperature equation is

$$dP/dz = 0.5Amv_e J_0^2 / ne^2 \quad (10.4)$$

where  $A$  is the area of the plasma. Also we have assumed no dc current, so there is no power input from dc fields. Other than rf, rather than dc power input, the dc electron temperature equation for the rf discharge is as in the dc case. Balancing the power input with the energy losses will give the overall electron density. However the losses are through the sheath, so to determine these losses, we have to model the sheath. We will also see that there is an additional power input, through the sheath, and into the plasma.

As we saw in the previous section, dc ion sheaths either involve Voltage drops of a few times the electron temperature and had a Debye length scale; or else, if the ion current is larger than the ion saturation current, is inherently collisional and had a much longer length scale. However the time dependent nature of the rf sheath allows additional flexibility in the nature of the sheath. Specifically, much larger potential drops can be generated while the plasma remains collisionless, somewhat analogous to PIII except the time dependence is now oscillatory. Thus an rf plasma allows for much higher energy ions to impinge on the workpiece, while, operating at lower neutral density.

We make the approximation that the rf frequency is much greater than the ion plasma frequency, so that the ions, even in the sheath do not respond to the rf fields, but react only to the dc fields set up. (Recall that the boundary condition is that there is no dc current; however as we will see, there are still large dc electric fields in the sheath.) The frequency is low enough that the electrons respond as if there were no time dependence. We assume further, that the dc potential drop across the sheath is very large compared to the electron temperature.

Let us say that the singular point of the quasi-neutral solution is at  $x=0$  and  $\phi=0$ , and the wall is at  $x=s_m$  at which point, there is a large negative dc potential. The actual time dependent potential between  $x=0$  and  $x=s_m$  is complicated due to the fact that the electrons oscillate back and forth between these positions. If the oscillating and dc potentials are large compared to  $T/e$ , as in fact we assume, the electron density is equal to the ion density to the left of the position where the instantaneous potential is zero, and is

zero to the right. Thus the picture of the sheath is that of an electron density whose edge oscillates between  $0 < x < s_m$  as the current oscillates through a cycle. The position of the sheath is at the instantaneous place where  $\phi=0$ . However, one can also define a potential averaged over an rf period; this is the potential that the ions respond to. If there were no electrons at all present in the sheath, the current, voltage and sheath width  $s_m$  would be related by the ion diode Langmuir-Child's law, Eq.(8.11). Because there are electrons in the diode region, the ion current is actually somewhat greater than this. However this does not specify the problem, because the specified quantities are  $J_0$ ,  $n_s$ ,  $T$  and the incident ion flow speed  $u_s = \sqrt{T/M}$ , the first of which is specified, the others all come from the outer, quasi-neutral solution. Thus the dc ion current density is specified, but not the Voltage or gap spacing. Furthermore, since there is no dc current, this ion current must be cancelled by an equal and opposite dc electron current.

The actual solution for the rf sheath was derived by Lieberman<sup>36</sup> by breaking the equations up into a time averaged potential which the ions respond to, and an exact part which the electrons respond to. We will not go through the nonlinear analysis of Ref.(36), but will give a very simple, but approximate solution which demonstrates the basic physics and scaling calculated by Lieberman. If the position of the sheath edge is denoted by  $s$ , then

$$J_0 \sin \omega t = n e ds/dt \quad (10.5)$$

as in Eq.(8.12). At  $t=0$ ,  $ds/dt=0$  and  $d^2s/dt^2 > 0$ , so the sheath is at plasma edge, the minimum value of  $s$ . Similarly, at  $t=\pi/\omega$ , the sheath is at the maximum position,  $s=s_m$ . In terms of the dc potential, the ion density as a function of  $\phi$  is given by

$$n = n_s (1 - 2e\phi/T)^{-1/2} \quad (10.6)$$

assuming  $u_i = u_s$  at  $\phi=0$ . Inserting this value of  $n$  into Eq.(10.5), and assuming that the potential is large compared to the temperature, we find that an approximate relation between  $s_m$  and  $\phi_m$  is

$$s_m = (e\phi_m/T)^{1/2} J_0 / n_s e \omega \quad (10.7)$$

which serves as one relation between potential drop, sheath width and plasma parameters. The other relation is simply the ion diode relation, Eq.(8.11). These two relations then specify the scaling laws for the sheath in terms of the oscillating current and the plasma parameters at the singular point of the quasi-neutral solution. The actual solutions that Lieberman finds from solving the nonlinear equations specifying the rf sheath are

$$J_i = 1.8 J_{LC} \quad (10.8)$$

where  $J_i = n_s e u_s$ , and  $J_{LC}$  is the current of the ion diode given by Eq.(8.11) but with diode Voltage given by  $\phi_m$ , and gap by  $s_m$ , and

$$s_m = (e\phi/1.6T)^{1/2} J_0 / n_s e \omega \quad (10.9)$$

Except for numerical factors of order unity, Lieberman's solution is equivalent to the approximated one we have derived here. This then allows us to calculate both the ion energy striking the surface as well as the ion energy flux out for the power balance calculation. From Eqs.(10.8 and 10.9), the Voltage drop across the sheath is given by

$$\phi_m(V) = 0.6 J_0^4 (\text{mA/cm}^2) / \{ T(\text{eV}) [n_s(\text{cm}^{-3}) / 10^{10}]^2 [f/13\text{MHz}]^4 \} \quad (10.10)$$

Since  $n$  is typically proportional to  $J_0$ , the dependence of  $\phi$  on  $J_0$  is not as rapid as it appears in Eq.(10.10). However the potential drop and sheath width still increase fairly rapidly with rf current  $J_0$ , so that as the current increases, collisions and the interactions with secondary electrons will become important.

We have calculated the dc ion current in terms of the plasma and circuit parameters. In order to insure that there is no net dc current, the dc ion current must be balanced an opposite electron current. Note that at time  $t = \pi/\omega$ , the electron sheath is in contact with the wall. Although the time of contact is short, the electron current to the wall during this time can be large because the electron thermal velocity is so much larger than the ion streaming velocity. Thus dc current is preserved at its zero value by the electrode drawing the necessary electron current for the time that the electron sheath is in contact with the electrode.

At time  $\pi/\omega$ , the actual Voltage across the sheath is equal to the dc potential  $\phi_m$ . Also,  $J$  is an odd function of time, and  $V$  is an even function of time, so the sheath is capacitive. If we define a sheath capacitance by

$$-AJ_0 \sin \omega t = C_s dV/dt \quad (10.11)$$

where  $A$  is the area of the electrode, and if  $V$  is approximated as  $\phi_m(1+\cos \omega t)/2$ , we can obtain the sheath capacitance, roughly equal to  $A/s_m$ , in terms of the plasma parameters.

In addition to the capacitive nature of the sheath, there is also a resistive part due to the fact that an individual electron incident on the sheath with velocity  $v_x$  bounces off with velocity  $v_x + 2ds/dt$ , where  $ds/dt$  is the velocity of the sheath. In calculating the energy flux bouncing off the sheath, we will only consider even powers of  $ds/dt$  since these are the portions that will not average to zero over an oscillation period. If we approximate the time average value of  $(ds/dt)^2$  to be  $0.5\omega^2 s_m^2$ , we find that the additional power input into the plasma is

$$P_{os} = 3An_s[e\phi_m/T]^{-1/2} m\omega^2 s_m^2 (T/2\pi m)^{1/2} \quad (10.12)$$

where in estimating the power input, we have assumed the average density of the sheath is  $n_s/(e\phi_m/T)^{1/2}$  to account for the density reduction as the ions accelerate through the sheath. This gives rise to a resistive part of the sheath response. Often this heating is called stochastic heating, since it is not related to plasma collisionality. This power input into the plasma must be added to the bulk resistive power input when calculating the energy balance. Notice however that this power is a total power in through the electrode. It is not put in uniformly along the plasma length as is the Ohmic heating. Thus, the longer the plasma, the less important this power input will be. If the stochastic heating is expressed in terms of  $J_0$ ,  $n_s$  and  $\omega$  only, the result is that the power input scales as  $J_0^4/n_s^2\omega^2$ , or if the power input is expressed in terms of  $\phi$ , it scales as  $\omega^2\phi_m$  independent of density and  $J_0$ .

Now let us consider the rf response of a symmetric planar discharge. There are two equivalent sheaths on the two equal area electrodes. The rf current is the same through out the plasma. Thus

while the sheath is moving towards one electrode, it is moving away from the other. For instance, while the sheath is in contact with the right hand electrode, and the voltage drop to the plasma zero; it has maximum separation from the left electrode and the voltage drop is at its maximum value, the full dc voltage drop. If the voltage drop across the sheath on the right is denoted  $V_r(t)$ , then the Voltage on the left hand sheath is given by  $V_l(t) = V_r(t - \pi/\omega)$ , so the total voltage drop across the plasma (assuming the sheath Voltage drops dominate) as a function of time is  $V_r(t) - V_r(t - \pi/\omega)$ .

To conclude, let us briefly discuss the case of an asymmetric discharge for which the areas of the two electrodes are not equal. The total rf current through the electrodes must be equal to one another. Thus  $jA$  is constant for each electrode. Then, according to Eq.(10.10), the potential drop across the sheath at an electrode of area  $A$  scales as  $A^{-4}$ , as long as the electron densities and temperatures are equal at each sheath. This rapid variation with area is typically not observed in experiments. Two reasons are that the sheath is collisional, and also that the densities are not the same at each electrode. This has been examined by Lieberman<sup>37</sup>, and depending on what the collisional law is (ie constant collision frequency, constant mean free path etc), there are different area scaling of Voltage. The collisionless, uniform density case has the most rapid scaling with electrode area. However even in the collisionless case, density differences at the electrodes can give rise to very different scaling laws. For instance, we have seen that the stochastic power input is proportional to  $\phi_m$  and independent of density and current. If this is the dominant power input, and the power is dissipated locally, from say local ionization or convection, then the power loss is proportional to  $n_s$ . Then  $n_s$  scales as  $\phi_m$ . Using this scaling in Eq.(10.10), we see that the potential drop at an electrode scale as  $A^{-4/3}$ , a much closer scaling to observation.

Summarizing, we have discussed four types of sheaths which can form in the processing plasma, the pure ion diode with at time dependent voltage pulse as is used for PIII, the Debye scale length sheath at the wall and anodes of dc plasmas, the collision and ionization sheath where the ion current exceeds the ion saturation current, and the rf sheaths which can be collisionless, but become collisional if the sheath width is great enough. The sheaths are responsible for the main plasma wall interaction, and we have

shown here how their properties can be calculated in various physics regimes.

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