Boundary Conditions for Adsorbing-Emitting Electrodes in Contact with Seeded, Dense Plasmas

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Adsorption and emission from boundary surfaces can profoundly alter the behavior of plasma-electrode systems, requiring a description that takes into account the physical characteristics of both the plasma and the surface. If the plasma is described in continuum terms, the surface properties enter through the specification of various species densities at the boundary, which strongly depend on the rates of emission of the respective species. Using the desorption rate expressions of Levine and Gyftopoulos for alkali metal coated metal surfaces, a method is proposed to determine boundary conditions for all species densities. The case of an equilibrium plasma confined between two plates is worked out in detail. The results suggest that ion densities could be very high near negatively biased boundaries, which in turn could lead to substantial field enhancement of thermionic electron emission. It is suggested that this mechanism might account for anomalously high currents observed in electrostatic probe studies.

Nomenclature

$\bar{c}_s$ = average thermal speed of s species
D = diffusion coefficient
e = absolute value of electron charge
E = electric field intensity
g = degeneracy of ground state
h = Planck's constant
j_s = current of s species
j = total current
k = Boltzmann's constant
l = half of distance between electrodes
m = particle mass
n = particle density
N = $4\pi n_{e0}\lambda_{D0}{}^3/3$
P_s = net rate of production of s species per unit volume
q = particle charge
T = absolute temperature
x = space coordinate perpendicular to electrode
α = degree of ionization
δ = thickness of Knudsen layer
ϵ_0 = permittivity of free space
φ = electrical potential
Φ_E = Schottky correction
Φ_s = desorption energy
Φ_w = surface work function
Γ = particle flux
μ = flux of particles moving towards surface
ν = flux of particles moving away from surface
$\bar{\nu}$ = frequency of oscillation of adatoms
λ = charged-neutral mean free path
λ_D = Debye length
ψ = defined in Eqs. (11) and (12)
σ_f = number of adsorption sites per unit area
θ = degree of coverage

Subscripts

a = atom
e = electron
i = ionization
j = electrode identification (= 1, 2)
p = ion
s = species identification (= e, p, a)
w = at electrode surface
$*$ = implies $E_w = 0$
0 = at $x = 0$

1. Introduction

ALKALI metal seeded plasmas are of interest from the viewpoint of several possible practical applications, due to the fact that in such plasmas reasonably high electrical conductivities can be achieved at relatively modest temperatures. As a result, the thermal requirements on the conducting or isolating walls of the plasma containing chamber or channel are far less severe than they would be for an unseeded gas of comparable conductivity. In fact, it is even possible to keep the walls at the desired plasma temperature and thereby produce a plasma very close to thermodynamic equilibrium throughout the container.

The engineering advantages gained are direct consequences of using an element of low ionization potential. This choice results in favorable bulk properties but it also inevitably complicates the nature of electrode surface-plasma interactions. This is seldom of great importance in experiments primarily concerned with the bulk behavior of the plasma, but it is a major factor in determining the sheath structure and electrode emission characteristics. The peculiarities of alkali metal vapor-metal surface interactions are being profitably utilized in thermionic converters and in ion engines using contact ionization, while they can be quite undesirable in some other situations. Relatively recent examples are failures of attempts to use electrostatic probes in dense seeded plasmas for the determination of ion density. The theory and technology of such probes is quite recent and their feasibility has been repeatedly demonstrated in unseeded, equilibrium plasmas.[1–5] Attempts to use them in seeded plasmas showed[6–8] that the current collected by negatively biased probes is a very strong function of the surface temperature and that the current may be much larger than what could be explained by thermionic emission of electrons from the probe. Neither fact is explained by theories that customarily assume the probe surface to be both nonemitting and fully adsorbing with respect to incident particles of either sign. No satisfactory explanation of these results seems to exist at this date, although there is general agreement that the observed anomalies must be due to some sort of seed-electrode interaction.

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The behavior of hot metallic surfaces in contact with alkali metal vapors has been extensively investigated in connection with thermionic converters and it is sufficiently well understood that no principal difficulty stands in the way of integrating reasonably realistic surface characteristics into a probe or a more general discharge theory. Admittedly, the mathematical difficulties are likely to be enormous, and numerical computations will be necessary.

To date, there has been a general tendency to treat the plasma at a high level of sophistication (e.g., Refs. 9 and 10) while making rather crude assumptions concerning the nature of the surface, which are acceptable in many cases, but totally inadequate for electrodes exposed to alkali metal seeded plasmas. The first serious attempt in this direction seems to be that of Bienkowski and Kalnavarns[11] who considered the effects of emission from the surface. They consider the emitted particle fluxes as freely specifiable boundary conditions, which is not the case for a realistic electrode, but it does render the computations manageable and represents a valuable contribution to the understanding of this complex subject.

The purpose of this paper is to clarify the boundary conditions to be satisfied on an emitting-adsorbing boundary exposed to an alkali metal seeded plasma, when the plasma is described in continuum terms. No attempt is made to solve the general problem so formulated, but a solution is given for the simple and instructive case of a plasma diode in complete thermodynamic equilibrium.

The motivation for this work stems from an interest in electrostatic probes, but the considerations apply to many electrode-plasma systems of other geometry or purpose and the paper will be phrased accordingly.

2. Description of the Plasma

In order to fix ideas, we shall consider a one-dimensional slab of plasma, bounded by two infinite, parallel, metallic surfaces. Since we are interested primarily in surface effects, we shall not consider certain complexities of the gas phase such as details of inelastic processes, temperature gradients, and radiation effects; rather we focus our attention on the ionization and recombination taking place on the electrode surfaces.

The plasma consists of a monatomic carrier gas which is completely unionized and all its atoms occupy their ground electronic state. In addition, a specified amount of alkali metal seed is present at a partial pressure below the saturation pressure determined by the temperature, so that the seed vapor is essentially superheated and no bulk condensation can take place on the walls. The temperature is taken to be high enough to result in appreciable degrees of ionization of the seed material. Excited states of both seed ions and atoms, as well as multiple ionization, are neglected. The degree of ionization is taken to correspond to equilibrium conditions as determined by the Saha equation. The fraction of seed material ionized may be high, but constrained by the requirement that the ion-ion or ion-electron collision frequency must be negligible compared to the electron-neutral collision frequency, including both seed and carrier gas atoms as neutrals.

The electron-neutral mean free path is small compared to the electrode spacing and the electric fields are moderate, so that ion, electron, and neutral particle fluxes can be properly described in terms of field independent transport coefficients and corresponding gradients.

The Debye length is much smaller than the electrode spacing, so that plasma properties are very nearly uniform throughout the interelectrode space. In particular, T is rigorously constant throughout; the plasma is isothermal. There is no applied or induced magnetic field. The plasma is in steady state. Since our model admits the possibility of particle loss to the wall, steady state can be maintained, in general, only if a gas phase production mechanism continuously replenishes the lost particles.

The governing equations express the conservation of mass and are written in one dimension[9]

$$d\Gamma_s/dx \equiv (d/dx)\{D_s[-dn_s/dx - (q_s/kT)n_s(d\varphi/dx)]\} = P_s \tag{1}$$

where Γ_s is the flux of the s species, D_s is the diffusion coefficient of s particles through neutrals, n_s is the number density and q_s is the charge of s particles, k is the Boltzmann constant, T the temperature (which is the same for all species), φ is the electrical potential and x is the position coordinate perpendicular to the boundaries. The subscript s may be taken as e for electrons, p for ions, and a for (seed) atoms. P_s is the net rate of production of s particles in the gas phase, assumed here simply as some known function of n_s and/or the densities of the other species. Since electrons and ions are created at the same rate, which is the same as the loss rate of atoms, we have $P_e = P_p = -P_a$.

The charges of the various species present are: $q_e = -e$, $q_p = e$, $q_a = 0$. The electrical potential is governed by Poisson's equation

$$d^2\varphi/dx^2 = (e/\epsilon_0)(n_e - n_p) \tag{2}$$

The available four equations determine the distributions of the three types of particle densities and the electric potential. The equation for seed atoms is conventionally omitted in most studies and the surface is assumed to be both nonemitting, and perfectly absorbing with respect to all charged particles. Taking $x = 0$ on the midplane between two electrodes $2l$ distance apart, the boundary conditions for the remaining set of three equations are usually chosen as follows:

$$\begin{gathered} n_e(-l) = n_e(+l) = 0 \\ n_p(-l) = n_p(+l) = 0 \\ \varphi(-l) = 0,\ \varphi(+l) = \text{specified} \end{gathered} \tag{3}$$

Conditions in Eq. (3) clearly represent a limiting case of more general conditions valid for both emitting and adsorbing surfaces. These more general conditions can be found only through a detailed consideration of surface characteristics.

3. Description of the Surface

Beginning with the work of Langmuir,[13] a great deal of effort has been extended to understand the behavior of alkali metal vapor-metal surface systems. This effort was essentially successful in that quantitative prediction of important effects is possible, and that predictions are reasonably well confirmed by experiment. In what follows, substantial use is made of the work of Gyftopoulos and Levine.[14–17] Along with some fundamentals, some of their results are summarized in this section, leaving out detailed justification which can be found in the original papers.

The essential feature of the surface-seed interactions is the large affinity between the alkali metal and the surface which results in partial or full monolayer coverage of the surface by the seed even if the partial pressure of the seed is well below the saturation pressure. It is known that practically all incident seed particles are adsorbed to the surface and that desorption takes place only after a certain amount of residence time. The most important parameter characterizing the coated surface is the degree of coverage (θ), defined as the ratio between the number of adsorbed atoms per unit surface area to the number of adsorption sites available per unit area. The value of θ strongly influences the rate at which electrons are emitted from the surface as well as the rates at which ions or atoms are desorbed.

The electron emission is governed by the surface work function, (Φ_w) which for a given substrate-adsorbate combination is determined solely by θ, provided the surface electric field is small. For a cesium-tungsten system, this relationship is given in Ref. 14 as

$$\Phi_{w*} = 4.62 - 2.81\{1 - (1 - 3\theta^2 - 2\theta^3) \times [1 - 2.6\theta(1 + 1.22\theta^{3/2})^{-1}]\} \quad (4)$$

where the * subscript refers to zero electric field at the wall. If the electric field at the surface (E_w) is large, the effective surface work function (Φ_w) has to be modified to take into account the Schottky effect

$$\Phi_w(\theta,E_w) = \begin{cases} \Phi_{w*}(\theta) - \Phi_E(E_w), & E_w < 0 \\ \Phi_{w*}(\theta) & E_w \geq 0 \end{cases} \quad (5)$$

where Φ_E is the Schottky correction to the work function, equal to $(-eE_w/4\pi\epsilon_0)^{1/2}$, ϵ_0 is the permittivity of free space, and E_w is considered positive if it points away from the solid.

The rate of the electron emission from the surface is given by the well-known Richardson-Dushman equation

$$\nu_{ew} = g_e 2\pi m_e(kT)^2 h^{-3} \exp(-e\Phi_w/kT) \quad (6)$$

where g_e is the degeneracy of the electron (=2), m_e is the electron mass, and h is Planck's constant. Note that the Schottky correction is taken to be zero for E_w non-negative, because in a retarding field the electrons sense a monotonically changing potential in passing from the solid into the plasma and hence there is no barrier whose magnitude would control the emitted electron flux. If $E_w \geq 0$, the surface will emit a flux corresponding to $\Phi_w = \Phi_{w*}$ while the external potential distribution determines what fraction of the emitted flux is returned to the surface, thus determining the net, measurable electron current.

The adsorbed seed particles share their valence electron with the substrate, so that they cannot properly be called either atoms or ions in their adsorbed state. Following Langmuir, they are called "adatoms." They may be desorbed either as atoms or as ions. The energies required to accomplish desorption (binding energies) in the absence of surface electric fields have been calculated in Ref. 15 for a cesium-tungsten system and the results can be fitted very closely by the following algebraic expressions:

$$\Phi_a = 2.880 - 2.643\theta + 1.780\theta^2 + 0.053\theta^3 - 0.320\theta^4 \quad (7)$$

$$\Phi_{p*} = 2.130 + 5.6266\theta - 1.5998\theta^2 - 7.467\theta^3 + 5.12\theta^4 \quad (8)$$

where the * subscript again indicates that Eq. (8) is valid for $E_w = 0$. It should be noted that the ion and atom binding energies are related to each other in a way which is derivable by a simple thought experiment as follows.[15] Consider that we desorb an adatom from the surface as an atom, a process for which we must supply Φ_a energy. Subsequently we ionize it by adding Φ_i energy and finally recuperate Φ_w energy by returning the electron to the solid. The net result is a desorbed ion and the net energy spent is Φ_p, given clearly by

$$\Phi_p = \Phi_a + \Phi_i - \Phi_w \quad (9)$$

We note that this argument applies whether or not the Schottky effect is included in the work function Φ_w. It immediately follows that the ion desorption energy in general will be dependent on E_w and related to the zero field ion desorption energy through

$$\Phi_p = \begin{cases} \Phi_{p*} + \Phi_E, & E_w < 0 \\ \Phi_{p*}, & E_w \geq 0 \end{cases} \quad (10)$$

The atom desorption energy is obviously independent of E_w.

The rates at which atoms or ions desorb (evaporate) from the surface are given in Ref. 16 by the following expressions in Arrhenius form:

$$\nu_{aw} = \bar{\nu}\sigma_f g_a \psi(\theta) \exp(-e\Phi_a/kT) \quad (11)$$

and

$$\nu_{pw} = \bar{\nu}\sigma_f g_p \psi(\theta) \exp(-e\Phi_p/kT) \quad (12)$$

where $\bar{\nu}$ is the characteristic frequency of vibration of the adsorbed adatoms, σ_f is the number of available adsorption sites per unit area on the metal surface, g_a, g_p are the statistical weights of the respective ground electronic states. The w subscript denotes conditions at the walls. The function $\psi(\theta)$ is given for any substrate and adsorbate metal combination approximately by

$$\psi(\theta) = \theta(1 - \theta)^{-1}(1 - \theta^{1/2})^{-1} \exp\{[\theta/(1 - \theta) + \theta^{1/2}/(1 - \theta^{1/2})]/2\} \quad (13)$$

The expression has been derived for a monolayer of adsorbed atoms and loses its validity as $\theta \rightarrow 1$, having neglected a possible second layer of adsorbed particles.

From Eqs. (9, 11, and 12) one can deduce the well-known Saha-Langmuir equation

$$\nu_{pw}/\nu_{aw} = g_p/g_a \exp[-e(\Phi_i - \Phi_w)/kT] \quad (14)$$

which shows that the desorbed adatoms are mostly ions if $\Phi_i < \Phi_w$ and mostly atoms if $\Phi_i > \Phi_w$. Both situations can occur in most systems, since Φ_w is above Φ_i for $\theta = 0$, whereas the opposite holds near $\theta = 1$, indicating that the surface may perform either as an ionizer of a neutralizer of incident particles, depending on the degree of coverage.

The rates of desorption and emission are assumed to be essentially independent of the rates of arrival of any species. This fact is rather important, since it controls the degree of coverage through a balance between adsorption and desorption, in a manner to be explained in the next paragraph.

We have now outlined the (differential) equations governing the plasma and the (algebraic) equations characterizing the surface with which the plasma is in contact. The two sets of equations must now be matched to obtain a solution which properly accounts for the behavior of both parts of the system.

4. Equilibrium System

Before the more general problem is considered, it is very instructive to work out the simple case of a system in perfect thermodynamic equilibrium. This implies constant temperature throughout the plasma and its boundary surfaces, as well as zero net fluxes for each of the three species. The net current, which is the difference between ion and electron currents, is then consequently also zero, corresponding to an open circuit operation of the diode. It follows that all properties of the system are determined by specifying the plasma composition, pressure, and temperature and that knowledge of plasma transport properties is not required, since there are no transport processes taking place.

Since perfect thermodynamic equilibrium implies Maxwellian velocity distribution for each species, and since collision integrals are identically zero for a Maxwellian distribution, the results are valid for any value of the mean free path.

Adsorption and desorption of all types of particles are allowed to occur on the boundaries according to the mechanisms described in the previous chapter, but only at exactly equal rates since otherwise perfect equilibrium could not exist. A de facto equivalent description of this condition is that ionization and recombination are allowed to occur on the walls at equal rates.

Volume ionization and recombination are also assumed to balance, so that these rates do not enter into the mass conservation equation of any species. The results thus are valid for any rate of ionization, including zero, so that we may set $P_s = 0$ in Eq. (1).

Artificial as it may seem, systems closely corresponding to the preceding description are experimentally realizable and have been investigated by several workers. A good review can be found in Ref. 18. Furthermore, the equilibrium behavior may serve as a point of departure for the study of slightly perturbed systems and therefore plays a singularly important role.

As assumed before, the spatial extent of the plasma is far larger than the Debye length, defined by $\lambda_D = (\epsilon_0 kT/e^2 n_{e0})^{1/2}$, where n_{e0} is the electron density at the midplane between the two electrodes. In equilibrium this condition guarantees the existence of a space charge neutral body of plasma away from the wall, since the electron and ion densities can differ only within a sheath of thickness $0[\lambda_D]$ near the walls.

The degree of ionization, α_0, is defined by

$$\alpha_0 = n_{p0}/(n_{p0} + n_{a0}) \tag{15}$$

where n_{a0} and n_{p0} are the seed atom and ion densities. For an equilibrium plasma, α_0 is given by Saha's equation approximately as

$$\alpha_0{}^2/(1 - \alpha_0) = g_p g_e g_a{}^{-1}(2\pi m_e kT)^{3/2}h^{-3} \times (n_{p0} + n_{a0})^{-1} \exp(-e\Phi_i/kT) \tag{16}$$

The 0 subscript is a reminder that Eqs. (15) and (16) are defined for the bulk of the plasma only.

The number densities of the charged species obey a Boltzmann distribution across the sheath:

$$n_a(x) = n_{a0} = \text{const} \tag{17}$$

$$n_e(x) = n_{e0} \exp(e\varphi/kT) \tag{18}$$

$$n_p(x) = n_{p0} \exp(-e\varphi/kT) \tag{19}$$

as follows from Eq. (1) for $\Gamma_s = 0$. The potential of the plasma is taken to be zero at $x = 0$.

The velocity distribution functions of all species are Maxwellian at all locations due to the assumed equilibrium. If we denote, as before, the flux of those s particles that move away from the wall as ν_s, we have then

$$\nu_s = n_s(8kT/\pi m_s)^{1/2}/4 \tag{20}$$

If the flux of particles moving towards the wall is denoted as $\mu_s(x)$, then the requirement of zero net flux yields

$$\nu_s(x) = \mu_s(x), \; s = a,p,e \tag{21}$$

In particular, this relation must be satisfied for $x = \pm l$, i.e., at the walls, where the ν_s fluxes are identical to the surface desorption (emission) rates as given in Sec. 2.

The neutral flux balance reads

$$\nu_{aw} = \mu_{aw} = \mu_{a0} \tag{22}$$

where the left-hand side is given by Eq. (11) and the right-hand sides by Eqs. (20) and (21). After some manipulation, we have

$$e\Phi_a(\theta)/kT + \ln\{\mu_{a0}[\tilde{\nu} g_a \sigma_f \psi(\theta)]^{-1}\} = 0 \tag{23}$$

For a given composition, temperature and plasma density, Eq. (23) provides an implicit determination of a (demonstrably unique) value of θ: the degree of coverage adjusts itself so that the desorbed atom flux just balances the arriving atom flux from the plasma. Since θ strongly influences charged particle emission rates, this explains why the neutral particles must be included in the considerations.

The ion flux balance reads

$$\nu_{pw} = \mu_{pw} = \mu_{p0} \exp(-e\varphi_w/kT) = \mu_{a0}\alpha_0(1 - \alpha_0)^{-1} \exp(-e\varphi_w/kT) \tag{24}$$

where the left-hand side is given by Eq. (12) and the rightmost expression by Eqs. (15), (19), and (21). After some algebra, we have

$$e\varphi_w/kT = e\Phi_p/kT + \ln\{\mu_{a0}[\tilde{\nu} g_p \sigma_f \psi(\theta)]^{-1}\} + \ln[\alpha_0(1 - \alpha_0)^{-1}] \tag{25}$$

or, using Eqs. (23) and (10)

$$e\varphi_w/kT = e(\Phi_{p*} - \Phi_a)/kT + e\Phi_E/kT + \ln[\alpha_0 g_p{}^{-1} g_a(1 - \alpha_0)^{-1}] \tag{26}$$

If $\Phi_E = 0$, this equation immediately determines the wall potential φ_w, which is seen to adjust itself in such a way as to result in an ion arrival rate which exactly balances the ion desorption rate at the value of θ determined by Eq. (21). While φ_w so obtained serves as a first approximation, Φ_E is not always zero and has yet to be determined. Since $\Phi_E \sim (E_w)^{1/2}$, this requires the determination of the electric field intensity at the wall, which usually cannot be done without computing the electric field distribution throughout the entire plasma. While quite complicated for nonzero currents, it can be done quite easily and exactly for an equilibrium plasma using Poisson's equation in connection with Eqs. (18) and (19)

$$(\epsilon_0/e)(d^2\varphi/dx^2) = n_{e0}[\exp(e\varphi/kT) - \exp(-e\varphi/kT)] \tag{27}$$

Setting $d^2\varphi/dx^2 = EdE/d\varphi$, this can be easily integrated to yield

$$(E_w{}^2 - E_0{}^2)^{1/2} = (8n_{e0}kT/\epsilon_0)^{1/2} \sinh(e\varphi_w/2kT) \tag{28}$$

from which, by some manipulation

$$\Phi_E \equiv (-eE_w/4\pi\epsilon_0)^{1/2} = (kT/e)8^{1/4}(3N)^{-1/2} \times [\sinh(-e\varphi_w/2kT)]^{1/2} \tag{29}$$

$$(\varphi_w < 0)$$

where we set $E_0 = 0$ and introduced the well-known plasma parameter, N, equal to the number of electrons within a sphere having a radius equal to the Debye length. We can now eliminate Φ_E from Eq. (26) to obtain an equation implicitly determining φ_w

$$e\varphi_w/kT = H(-\varphi_w)8^{1/4}(3N)^{-1/2}[\sinh(-e\varphi_w/2kT)]^{1/2} + e(\Phi_{p*} - \Phi_a)/kT + \ln[g_a\alpha_0 g_p{}^{-1}(1 - \alpha_0)^{-1}] \tag{30}$$

where $H = 1$ for φ_w negative and $H = 0$ for φ_w positive, reflecting the range of validity of Eq. (5).

So far we have used the conditions that the net atom and ion fluxes at the wall be zero, which proved to be sufficient to determine θ, φ_w and Φ_E, i.e., all unknowns of interest. The question may then be raised as to the meaning of zero net flux condition [see Eq. (21)] for electrons, which appears to be superfluous. Closer investigation using Eqs. (6, 9, and 26) shows that it is indeed redundant and can be safely ignored.

It is now possible to calculate all properties of our system. The degree of coverage follows from Eq. (23), the floating potential from Eq. (30), the Schottky correction from Eq. (29), and the emitted electron current from Eq. (6). These quantities have been calculated for a cesium-tungsten system and are shown on Figs. 1–4. ($\sigma_f = 4.8 \times 10^{18}$ site/m^2 and $\tilde{\nu} = 10^{12}$ sec^{-1} were used.)

The charged particle densities at the wall ($x = \pm l$) can be calculated from Eqs. (18) or (19) using the floating potential values from Fig. 2. The electron density could also be calculated from the formula

$$n_{ew} = 4\nu_{ew}/\bar{c}_e = 4j_{ew}/\bar{c}_e e, \; \bar{c}_e = (8kT/\pi m_e)^{1/2} \tag{31}$$

where j_{ew} is given on Fig. 4.

These calculations differ from the results of Ref. 17 in two respects. We assumed thermodynamic equilibrium, which determines a unique floating potential and a unique coverage, whereas in Ref. 17 steady state was stipulated and φ_w was taken highly negative. It was then found that under certain conditions steady state could occur at more than one value of θ, which admits the possibility of hysteresis effects. The second difference lies in taking into account the Schottky effect, neglected in Ref. 17.

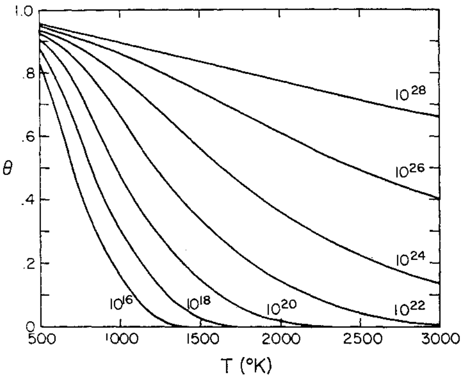

Fig. 1 Degree of coverage for a tungsten wall exposed to a cesium seeded plasma in equilibrium. Parameter is seed density ($n_{ao} + n_{po}$, m^{-3}).

A close comparison between Figs. 1 and 2 reveals that for any given density, the maxima of the φ_w curves always correspond to roughly $\theta \approx 0.6$, the first zeros to $\theta \approx 0.3$ and the minima to $\theta \approx 0.03$. This connection provides a clue to the qualitative explanation of the tendencies exhibited in Fig. 2.

We note first that by Eqs. (6) and (12) $\nu_{ew}/\nu_{pw*} \sim \psi^{-1}T^2 \exp[-e(\Phi_w - \Phi_{p*})/kT]$, and that ψ,Φ_w,Φ_{p*} are all functions of θ. As the temperature increases and concurrently θ drops from its high value at $T = 500°$K, the electron to ion current ratio increases at first because $\psi(\theta)$ drops sharply for θ values larger than about 0.6 (Eq. 13). The relative increase of electron emission must be matched by an increased electron arrival rate to the surface which means that φ_w has to adjust itself to be the positive, electron attracting surface potential shown for this range. The $\psi(\theta)$ function is fairly flat for $\theta \lesssim 0.6$, so that the θ dependence of $(\Phi_w - \Phi_{p*})$ in the exponential will take over control of the behavior at temperatures above the value corresponding to $\theta \cong 0.6$. Examination of Eqs. (4) and (8) shows that $\Phi_w - \Phi_{p*}$ is negative for $\theta \gtrsim 0.2$ and positive for smaller θ values. This means that as soon as the exponential factor begins to dominate, the electron current will drop with temperature, the decrease being made even sharper by the fact that not only e/kT, but $|\Phi_w - \Phi_{p*}|$ itself decreases. The reduced electron current requires a reduction of the electron arrival rate, which means that the surface potential has to be electron repellant, i.e., negative.

If the coverage drops below 0.2, $\Phi_w - \Phi_{p*}$ changes sign and further temperature increase leads to indefinite increase of the electron-ion emission rate ratio and to a monotonically increasing surface potential, as shown on Fig. 2. (The minimum of the φ_w curve does not correspond exactly to the $\Phi_w - \Phi_{p*} = 0$ condition because of the minor "modulation" caused by the $\psi^{-1}T^2$ coefficient.)

Figure 3 is a plot of ν_{ew}/ν_{ew*}, the ratio of actually emitted electron flux to the flux that would have been emitted without the Schottky effect. This factor is not too large, but it can be nearly two under certain circumstances, and therefore cannot be completely ignored.

There are reasons to believe that even a slightly more negative wall potential (and hence a small deviation from equilibrium) would be sufficient to increase this factor considerably. This can be seen by recalling that θ was determined by the neutral flux balance, which would not be directly influenced by an externally enforced lowering of φ_w, so that θ and the binding energies should not differ much from their equilibrium values. On the other hand, Eqs. (5, 6, and 29) show that for large values of $(-e\varphi_w/kT)$

$$\nu_{ew}/\nu_{ew*} = \exp(e\Phi_E/kT) \sim \exp[\exp(-e\varphi_w/4kT)] \quad (32)$$

which is an extremely sharp dependence on φ_w indeed. This sharpness is illustrated by the sizeable ν_{ew}/ν_{ew*} ratios of Fig. 3, into which the minute differences between the solid and dashed lines of Fig. 2 are translated. This is a good indication that the large currents collected by negatively biased probes in seeded plasmas might well be caused by the Schottky effect.

The largeness of this effect is closely associated with the ion-emission properties of the surface. The large ion emission rates allow a near-equilibrium ion density distribution function throughout the sheath, in that there is only a slight imbalance between forward and backward particle fluxes. Contrary to the perfectly absorbing wall near which the charged particle density is very low, the ion density at a negative wall in a near-equilibrium situation can be several orders of magnitude larger than its value in the plasma (n_{i0}), as indicated by Eq. (19). The large positive space charge then leads to a high electric field at the wall, which can be sufficiently intense to give rise to field emission.

It is worth noting that at negative φ_w values the random ion current at the wall ($n_{iw}\bar{c}_i/4$) may be much larger than the random electron current, on account of the high ion density n_{iw}. This implies that in such cases it is possible to pass relatively large ion currents through the sheath while the ions still retain a very nearly Maxwellian velocity distribution.

5. Diode with Nonzero Currents

If the potential of the boundary is different from the floating potential specified by Eq. (30), then a net flux of each species will exist throughout the diode. In the presence of production terms P_s, they will generally vary with x. At the walls, they can be expressed as

$$\Gamma_{sj} = (\mu_{sj} - \nu_{sj})(-1)^j, \; s = e,p,a \quad (33)$$

where $j = 1, 2$ refer to the electrodes at $x = x_1 = -l$ and $x_2 = +l$, respectively. The jth power of -1 accounts for the fact that Γ_s is defined to be positive if it points along $+x$, while ν is traditionally taken positive if pointing away from the wall.

The externally measurable, total current is

$$j = e(\Gamma_p - \Gamma_e) \quad (34)$$

which is independent of x due to the fact that $P_e = P_p$, i.e., that electrons and ions are always produced in equal numbers.

We shall assume that surface processes are characterized by the relations of Sec. 1 as they were for the equilibrium system. The characterization of the gas phase, on the other hand, is now clearly far more complex due to the presence of transport processes: diffusion and electrical conduction definitely has to be included [Eq. (1)], whereas thermal conduction, thermal diffusion, and electron-heavy particle

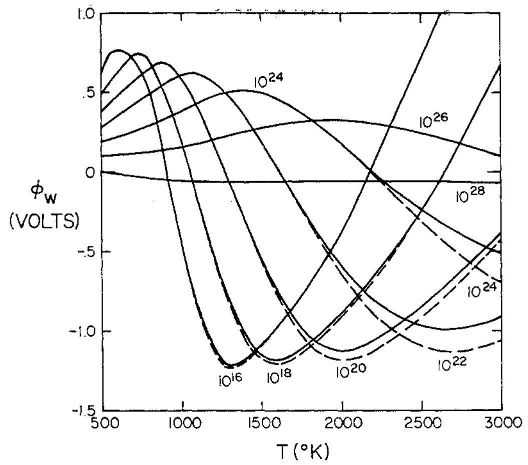

Fig. 2 Floating potential for a tungsten wall at equilibrium coverage, for various seed densities. Dashed lines include Schottky effect, solid lines do not.

collisional energy transfer may or may not be taken into account, depending on the level of sophistication desired. Since the present paper concerns itself with the boundary conditions, and not with the solution of the entire problem, we shall choose the simplest possible model that is still adequate for the demonstration of the principles involved. We shall assume that the gas and the surfaces are at a constant temperature and that no chemical reactions take place within the sheath. The first condition may describe a relatively unimportant case since most plasmas are confined by cold walls; nevertheless it is experimentally realizable. The second condition requires that the sheath be thinner than some appropriate mean free path, probably the electron-neutral free path for ionization by electron impact. Production is allowed in the bulk of the gas.

The plasma behavior under these conditions is governed by the three Eqs. (1) and (2), which must, of course, be supplemented by appropriate boundary conditions. In our case, this would amount to the specification of all species densities at both walls, as well as the electrical potential at both walls. This could be done easily if the surface coverage θ would be known, which in the equilibrium case could be determined by equating the atom desorption rate ν_{aj} to the atom arrival rate μ_{aj}. If nonzero net fluxes Γ_{sj} are present, this method will no longer work and there is no simple way to calculate the ν_{sj} and μ_{sj} fluxes separately. If the deviation from the Maxwellian is slight, the following approximate method should produce reasonable results.

Consider a layer extending from the boundary having a thickness (δ) of several s species-neutral atom mean free paths (Knudsen layer). At the outer edge of this layer, continuum relations hold, hence the net flux is given by Eq. (1). The layer is assumed to be very thin compared to the curvature of the boundary surface, so that its structure is effectively one-dimensional. By reasons of continuity in the absence of chemical reactions, Γ_s is then constant across this layer, so that the continuum expression for Γ_{sj} can be equated to the microscopic expression of the net flux at the surface, as given by Eq. (33). We can write

$$\Gamma_{sj} = [-\nu_{sj}(\theta_j) + \mu_{sj}](-1)^j = D_s[-dn_s/dx - (q_s n_s/kT)(d\varphi/dx)]_j \quad (35)$$

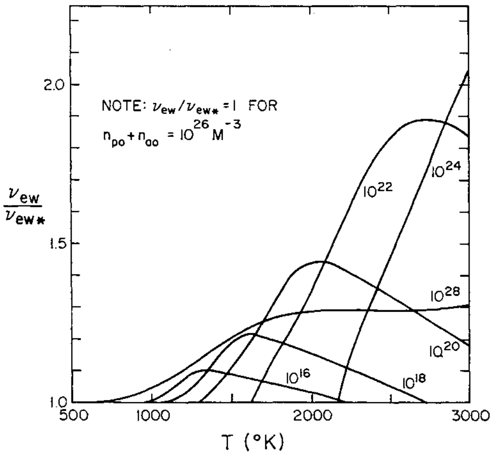

Fig. 3 Ratio of electron fluxes emitted with and without Schottky effect from a tungsten wall under equilibrium conditions, for various seed densities.

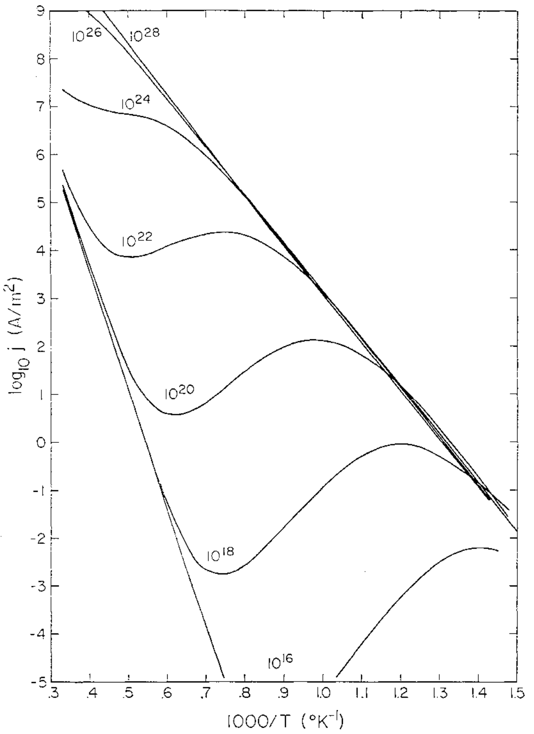

Fig. 4 Electron current emitted from a tungsten wall under equilibrium conditions, taking the Schottky effect into account. Parameter is seed density.

The arrival rate to the wall, μ_{sw}, cannot be determined from the information assumed to be given this far; a new relation of some sort is required. This may be obtained by making the assumption that the density of the s species does not change appreciably across the Knudsen layer, even though the shape of the distribution function may change considerably to adapt itself to the given boundary conditions. This assumption is consistent with the constancy of the diffusion coefficient D_s; they are both valid if the energy gained by the charged particle between two subsequent collisions is small compared to its thermal energy. In such a case, there can be no appreciable density change due to retardation within one free path, as the following simple calculation shows:

$$|\Delta n/n| \approx |n^{-1}(dn/dx)_w|\delta \approx |n^{-1}d[n_0 \exp(e\varphi/kT)]/dx|_w\delta = (e/kT)|d\varphi/dx|_w\delta = e|E_w|\delta/(kT) \approx (e|E_w|\lambda/kT) \ll 1, \text{ by definition} \quad (36)$$

where we used the equilibrium density distribution of Eq. (18), which incorporates the retardation effect exactly under equilibrium conditions.

The continuum expression for the density at the outer edge of the Knudsen layer is n_{sj}. A microscopic expression for the density at the wall is obtained by assuming that both ν and μ form half-Maxwellian distributions at the same temperature, but different densities. Equating the two, we have

$$n_{sj} = 2[\nu_{sj}(\theta_j) + \mu_{sj}]/\bar{c}_s \quad (37)$$

Eliminating the unknown μ_{sj} between Eqs. (35) and (37), we can write

$$n_{sj} = 2[2\nu_{sj}(\theta_j) + (-1)^j\Gamma_{sj}]/\bar{c}_s \quad (38)$$

or, after eliminating Γ_{sj} by Eq. (1)

$$n_{sj} + (-1)^j(2D_s/\bar{c}_s)(dn_s/dx)_j = [4\nu_{sj}(\theta_j) + (-1)^j(2D_s q_s n_s/kT)(d\varphi/dx)_j]/\bar{c}_s \quad (39)$$

From the viewpoint of the continuum problem, the outer edge of the Knudsen layer coincides with the electrodes themselves so that Eqs. (38) or (39) represent the desired boundary conditions for $n_s(x)$, $s = e, p, a$ and $j = 1, 2$.

Equation (39) shows the complexity of the boundary conditions to be imposed in our problem: the conditions for various species are of the mixed type, coupled through θ_j and in addition each is dependent on the potential gradient at the electrodes in a nonlinear fashion.

The solutions of our four second-order governing equations contain eight constants of integration, whereas there are six conditions following from Eq. (39). Since θ_1 and θ_2 are also unknowns, we seem to have a set of four freely adjustable parameters. However, one additional boundary condition is obtained from the following consideration. If the surface-plasma system is in steady state, there is no steady accumulation of seed particles at the wall and hence, the net flux of heavy particles to the wall must be equal to the net flux of heavies away from it

$$\nu_{aj} + \nu_{pj} = \mu_{aj} + \mu_{pj}$$

which can be rewritten as

$$\Gamma_{aj} = \nu_{aj} - \mu_{aj} = -(\nu_{pj} - \mu_{pj}) = -\Gamma_{pj} \tag{40}$$

If there is a net ion current collected at the wall, then there must be a net flux of atoms leaving the wall, necessarily accompanied by a neutral atom density gradient. This fact rather explicitly points out the need for considering the diffusion of neutral seed particles; this process is an integral part of the over-all behavior of the system.

Since $P_a = P_p$, it can be easily shown from Eq. (1), that $\Gamma_{p1} + \Gamma_{a1} = \Gamma_{p2} + \Gamma_{a2}$, hence Eq. (4) is actually only one condition, even though it may be applied at either electrode.

Since the electrons are able to pass in or out of the metal, no statement analogous to Eq. (42) can be made with regard to the net electron flux Γ_e.

Eventually we are left with only three freely specifiable parameters for the problem, which could be taken as the two electrode potentials and any one particular density at either one of the electrodes. All other quantities are determined as solutions of the problem.

It should be noted that at the outset we have taken the seed and background gas type as given, while diode spacing and electrode materials were also considered to be specified. The background gas density influences the transport properties only and can be eliminated from the mathematics by appropriate normalization. All these factors are fixed in our problem, whereas experimentally they are certainly freely variable (within limits). The mentioned three degrees of freedom correspond to the experimental variation of seed concentration and plate potential difference.

Equation (34) shows that the measurable current may be zero if equal ion and electron net fluxes flow to the walls, representing ambipolar diffusion, which tends to deplete the charged particle population in the diode. This phenomenon is accounted for in the present formulation: the ambipolar diffusional fluxes would be part of and incorporated in the solutions.

In many systems temperature variations may be quite important, which means that the T = const assumption must be replaced by some form of the energy equation either for the plasma as a whole or for the heavy and light species separately. Boundary conditions for the species temperatures could be derived by methods analogous to those used here. This topic has not been investigated: it suggests a logical direction for further work. The procedure discussed in this section probably remains appropriate for the determination of densities at the wall even if T is variable.

It is beyond the scope of this paper to attempt a solution of the problem as formulated in this section. It is clear that it is very complex and that the possibility of analytical solutions seems extremely remote. Numerical solutions should be obtainable and would be expected to shed some light on the peculiar behavior of alkali metal coated electrodes. In particular, they would be expected to show large Schottky effects at the cathode. This effect was seen to be moderate under equilibrium conditions where a moderate wall potential prevails, but for reasons given in Sec. 3, they are expected to be far larger for wall potentials below the floating value.

6. Summary

The paper presents a short review of the physics of alkali metal coated solid surfaces. In particular, expressions are quoted for desorption rates of heavy particles and for emission rates of electrons. Arrival rates of all particles are given exactly for a system in equilibrium while in the more general case of nonzero currents the net particle fluxes are expressed in terms of gradients of plasma properties. In the possession of this information, boundary conditions for particle densities are formulated which in essence express the principles of conservation of mass and charge across the plasma-solid interface. The general form of these conditions, valid for an isothermal system with nonzero currents, is given by Eqs. (39), to be complemented by Eq. (40). The problem posed by Eqs. (1) and (2) and the aforementioned boundary conditions is extremely complex; its solution for a general case was not attempted. If perfect thermodynamic equilibrium exists, the problem greatly simplifies and a solution can be obtained, the results of which have been given.

References

[1] Pollin, I., "The Stagnation Point-Langmuir-Probe in a Shock Tube, Theory and Measurements," *The Physics of Fluids*, Vol. 9, 1964, pp. 1433–1445.

[2] Laird, J. D., "The Measurement of Ion Densities with a Flat Plate, Continuum Langmuir Probe in a Shock Tube," *Proceedings of the 7th International Conference on Phenomena in Ionized Gases*, Vol. III, Beograd, 1966, pp. 45–47.

[3] Burke, A. F., "Electrical Currents to a Flat Plate in Supersonic Ionized Flow," AIAA Paper 68-166, New York, 1968.

[4] de Boer, P. C. T. and Johnson, R. A., "Flat Plate Probe for Measuring Ion Density," AIAA Paper 68-165, New York, 1968.

[5] Hoppmann, R. F., "Cold Electrode Characteristics in Shock Ionized Air Plasmas," *The Physics of Fluids*, Vol. 11, 1968, pp. 1092–1110.

[6] Turcotte, D. L. and Friedman, W., "Electrode Interactions in Seeded Combustion Products," *Tenth Symposium (International) on Combustion*, 1965, pp. 673–683.

[7] Wolf, R. J., "Electrode Effects in a Seeded Plasma," *AIAA Journal*, Vol. 4, No. 12, Dec. 1966, pp. 2155–2159.

[8] McKee, H. B., "Electrostatic Probe Theory and Application in a High Temperature, Collision Dominated, Potassium Seeded Argon Plasma," SU-IPR Rept. 137, 1967, Stanford Univ.; also *AIAA Journal*, Vol. 6, No. 8, Aug. 1968, pp. 1587–1589.

[9] Chung, P. M., "Electrical Characteristics of Couette and Stagnation Boundary-Layer Flows of Weakly Ionized Gases," *The Physics of Fluids*, Vol. 7, 1964, pp. 110–120.

[10] Burke, A. F. and Lam, S. H., "A General Theory of Weakly Ionized Gas Flows Including Compressibility and Electron Energy Effects," AIAA Paper 67-100, New York, 1967.

[11] Bienkowski, G. and Kalnavarns, J., "The Effect of Surface Emission on Continuum Electrostatic Probe Theory," AIAA Paper 68-167, New York, 1968.

[12] Wasserstrom, E., Su, C. H., and Probstein, R. F., "Kinetic Theory Approach to Electrostatic Probes," *The Physics of Fluids*, Vol. 8, 1965, pp. 56–72.

[13] Taylor, J. B. and Langmuir, I., "The Evaporation of Atoms, Ions, and Electrons from Caesium Films on Tungsten," *Physical Review*, Vol. 44, 1933, pp. 423–458.

[14] Gyftopoulos, E. P. and Levine, J. D., "Work Function Variation of Metals Coated by Metallic Films," *Journal of Applied Physics*, Vol. 33, 1962, pp. 67–73.

[15] Gyftopoulos, E. P. and Levine, J. D., "Adsorption Physics of Metallic Surfaces Partially Covered by Metallic Particles. I. Atom and Ion Desorption Energies," *Surface Science*, Vol. 1, 1964, pp. 171–193.

[16] Gyftopoulos, E. P. and Levine, J. D., "II. Desorption Rates of Atoms and Ions," *Surface Science*, Vol. 1, 1964, pp. 225–241.

[17] Gyftopoulos, E. P. and Levine, J. D., "III. Equations of State and Electron Emission S-Curves," *Surface Science*, Vol. 1, 1964, pp. 349–360.

[18] Dewey, F. C., "A Unified Treatment of Sheath Problems in Alkali Plasma Devices," AIAA Paper 67-691, Anaheim, Calif., 1967.