THE EQUILIBRIUM DISTRIBUTION OF POTENTIAL AND OF ELECTRONS OUTSIDE THE SURFACE OF A CONDUCTOR

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Abstract

The potential distribution due to space charge in the neighborhood of a plane conducting surface is derived for the case of equilibrium under zero applied field and under retarding fields, by use of Poisson's equation and the Boltzmann distribution law, which is extended to include application to the Fermi-Dirac statistics. The electron density is likewise evaluated as a function of the distance from the surface. In both cases an applied electric field has no appreciable effect within a certain critical distance which is dependent upon the field. Assuming degeneracy within the conductor the electron atmosphere is also degenerate near the surface, becoming entirely classical at distances greater than 2 or 3×10^{-7} cm. Its density is independent of the nature of the conductor and at a given distance is directly proportional to the absolute temperature. The potential at a given distance is characteristic of the conductor and varies only slightly with temperature, while its magnitude is consistent with the Sommerfeld electron theory. The field intensity equals that computed from an image force law at distances in the neighborhood of 3×10^{-7} cm, depending upon temperature, and is increasingly greater than the latter at greater distances. The mean electron separation distance in a plane parallel to the surface is comparable with the distance of this plane from the surface.

IN A recent paper[1] R. S. Bartlett and the author pointed out that the conception of electrons within a conductor as a degenerate gas obeying the Fermi-Dirac statistics reopens the matter of the effect of space charge upon the thermionic work function. The general consequences were mentioned of an explanation of the work function based entirely upon space charge instead of the usual image force, and in a later paper Bartlett[2] has on this basis computed the potential distribution and the thermionic current density between plane parallel electrodes for the case of an applied field and for accelerating fields. The results show a work function of the correct order of magnitude and a variation of current with applied field of the correct general form, thus indicating that a space charge origin of the work function may be used to explain the Schottky effect. It is noteworthy that Bartlett is able from this point of view to derive a single curve for the thermionic current which is valid continuously from zero applied field through strong applied fields, and which therefore includes both the familiar Child's equation and the Schottky equation under one explanation.

It is the purpose of this paper to examine the equilibrium distribution of potential and electron concentration outside the surface of a plane elec-

[1] R. S. Bartlett and A. T. Waterman, Phys. Rev. **37**, 279 (1931).
[2] R. S. Bartlett, Phys. Rev. **37**, 959 (1931).

trode in the presence of retarding electric fields (including zero field). This is accomplished by solving Poisson's equation in conjunction with the Boltzmann distribution law (generalized to apply to the Fermi-Dirac statistics) after the manner in which this was done for the purely classical case by Langmuir.[3] The generalized distribution law referred to is

$$A = A_0 e^{-(V-V_0)\epsilon/kT} \tag{1}$$[4]

where A and A_0 are the Fermi A's[5] corresponding to two small regions about points P and P_0 in the electron gas where the potentials are V and V_0 respectively. In the present case P_0, A_0 and V_0 will refer to the interior of the conductor. A deviation of Eq. (1) follows from equality (in equilibrium) of the number of electrons per unit area per second proceeding from P_0 to P against the potential difference $V-V_0$, and of the electron current density leaving P in the opposite direction. Thus, taking u as the velocity component in the direction P_0P, the number of electrons reaching P per unit area per second, calculated in the usual kinetic theory manner, is

$$\nu_1 = \frac{\pi G}{a}\left(\frac{m}{h}\right)^3 \int_{u'}^{\infty} u(\log A_0 e^{-au^2} + 1)du$$

where $a = m/2kT$, $A_0 =$ Fermi A at P_0, $\frac{1}{2}mu'^2 = (V-V_0)\epsilon$, or

$$\nu_1 = \frac{\pi G}{2a^2}\left(\frac{m}{h}\right)^3 \int_0^{e^{-au'^2}} \frac{\log (A_0 y + 1)}{y} dy. \tag{2}$$

The number of electrons about P striking unit area per second is the similar expression integrated from 0 to ∞, or

$$\nu_2 = \frac{\pi G}{2a^2}\left(\frac{m}{h}\right)^3 \int_0^1 \frac{\log (Ay + 1)dy}{y} \tag{3}$$

where A refers to the region about P. Both (2) and (3) are valid whether the gas is classical or degenerate.

For equilibrium, $\nu_1 = \nu_2$ and

$$\int_0^{e^{-au'^2}} \frac{\log (A_0 y + 1)dy}{y} = \int_0^1 \frac{\log (Ay + 1)dy}{y}$$

If

$$f(A, y) = \int \frac{\log (Ay + 1)dy}{y},$$

this condition is satisfied when

$$f(A_0, e^{-au'^2}) = f(A, 1). \tag{4}$$

[3] Langmuir, Phys. Rev. **21,** 419 (1923).

[4] Cf. Waterman, Phys. Rev. **35,** 668 (1930); Bartlett: reference 2, p. 963.

[5] Defined by

$$n = \frac{2\pi G(2mkT)^{3/2}}{h^3} \int_0^{\infty} \frac{u^{1/2}du}{\frac{1}{A}e^u + 1}$$

$f(A, y)$ may be evaluated by series expansions both for $Ay<1$ and for $Ay>1$, when it is seen that (4) is satisfied in both cases, term for term, provided $A = A_0 e^{-au'^2} = A_0 e^{-(V-V_0)\epsilon/kT}$.

For both A and A_0 classical ($A = [nh^3/G(2\pi mkT)^{3/2}]$, n being the electron concentration), Eq. (1) becomes the familiar Boltzmann equation:

$$n = n_0 e^{-(V-V_0)\epsilon/kT}. \tag{1a}$$

For both A and A_0 degenerate ($\log A = \zeta/kT$, ζ being the thermodynamic potential):

$$\zeta = \zeta_0 - (V - V_0)\epsilon. \tag{1b}$$

For A classical and A_0 degenerate:

$$n = \frac{G(2\pi mkT)^{3/2}}{h^3} e^{\zeta_0 - (V-V_0)\epsilon/kT}. \tag{1c}$$

It may be noted in passing that Eq. (1) finds several labor-saving applications. Just as, in the form (1a) it has commonly been used to derive the thermionic saturation current density resulting in the $T^{1/2}$ equation, similarly in the form (1c) it results in the Sommerfeld T^2 law. In the form (1b) it gives directly the Volta P.D. between two metals or, as Becker has aptly named this quantity to distinguish it from the contact P.D., the junction P.D.

Potential Distribution

We proceed to the derivation of the equilibrium conditions in the neighborhood ($x>0$) of a metal whose surface lies in the plane $x=0$, in the presence of a uniform electric field in the x-direction which retards electron emission. Assuming the electron gas degenerate within the metals, then for points far enough from the surface so that the gas is effectively in the classical state, Eq. (1c) applies, whence by use of Poisson's equation,

$$\frac{d^2V}{dx^2} = \frac{4\pi G\epsilon(2\pi mkT)^{3/2}}{h^3} e^{\zeta_0 + (V-V_0)\epsilon/kT} \tag{5}$$

where $\epsilon = |\epsilon|$, the charge on an electron.

Performing the first integration subject to the boundary condition that at $x=\infty$, $V=-\infty$, $dV/dx = E$:

$$\left(\frac{dV}{dx}\right)^2 = \beta^2 e^{(V-V_0)\epsilon/kT} + E^2 \tag{6}$$

$$\text{where} \quad \beta^2 = \frac{8\pi G\epsilon(2\pi m)^{3/2}(kT)^{5/2}}{h^3} e^{\zeta_0/kT}. \tag{6}$$

The general solution of Eq. (6), subject to the boundary condition that at $x=0$, $V=V_0$,[6] is

[6] Strictly speaking on account of the penetration of surface, $x=0$ must be a plane a short distance within the conductor, if V_0 is to mean the normal intrinsic potential of the metal. The distance involved is of the order of atomic dimensions (cf. Waterman: Proc. Roy. Soc. **A121,** 28 (1928).

$$x = \frac{kT}{\epsilon E}\left(\log\frac{(y^2+\alpha^2)^{1/2}+\alpha}{(y^2+\alpha^2)^{1/2}-\alpha} - \log\frac{(1+\alpha^2)^{1/2}+\alpha}{(1+\alpha^2)^{1/2}-\alpha}\right)$$

where $\alpha = E/\beta$, $\log y = (V - V_0)\epsilon/kT$,
or

$$x = \frac{kT}{\epsilon E}[\log(1 + 2z^2 + 2z(1+z^2)^{1/2}) - \log(1 + 2\alpha^2 + 2\alpha(1+\alpha^2)^{1/2})] \quad (7)$$

where $z = \alpha/y$.

Since, assuming one electron per atom in the conductor, β is of order of magnitude 10^{10} or more for thermionic emitters, $\alpha \ll 1$ for all practicable applied fields, and the second logarithm in Eq. (7) may be expanded in powers of α. Similarly the first logarithm may be expanded in powers of z or of $1/z$, depending upon whether $\alpha <$ or $> y$. We have therefore as approximate solutions in a more usable form:

For

$$|V - V_0| > \frac{kT}{\epsilon}\log\frac{E}{\beta}, \quad (z > \alpha):$$

$$V - V_0 = -\frac{2kT}{\epsilon}\log\frac{\epsilon\beta}{2kT}x \quad (8)$$

for

$$\frac{\epsilon\beta}{2kT}x \gg 1$$

i.e. $x > 10^{-10}$ cm approx.

For

$$|V - V_0| < \frac{kT}{\epsilon}\log\frac{E}{\beta}, \quad (z < \alpha):$$

$$V - V_0 = -Ex + \frac{kT}{\epsilon}\log\frac{4E^2}{\beta^2}. \quad (9)$$

Thus in the region covered by Eq. (8) the applied field does not affect the potential distribution, while in the region where Eq. (9) is valid space charge effects are absent. The boundary between the two is quite narrow in range, and the critical distance from the surface is

$$x' = \frac{kT}{\epsilon E}\log(3 + 2(2)^{1/2}) = 1.52 \times 10^{-4}T/E \text{ cm } (E \text{ in } v/cm,\ T \text{ in } °K),$$

the distance at which

$$z = \alpha, \text{ or } |V - V_0| = kT/\epsilon \log E/\beta.$$

Fig. 1 shows the potential difference $(V_0 - V)$ between the interior of the metal and external points as a function of the distance x, for the case of tungsten at 2300°K. The solid line represents the case of no applied field, and agrees with that of Bartlett[7] derived in a different manner. The

[7] Bartlett, reference 2, Fig. 3.

broken lines show the effect of various applied fields, from 3v/cm to 3×10^7 v/cm. The main curve is not carried closer to the surface than about 3×10^{-7} cm, for within this region the electron gas begins to be degenerate and the premise of this calculation (Eq. 1c) is not applicable. It will be noted that at ordinary electrode distances the potential difference between interior and exterior is of an order of magnitude in agreement with the work function on the Sommerfeld theory. It is of interest further to remark that retarding fields of cold extraction magnitude affect the potential distribution at points so close to the surface that the electron gas becomes degenerate. If accelerating fields do likewise the conjecture may be ventured that herein lies a form of physical explanation for the slightness of temperature effect on cold extraction currents.

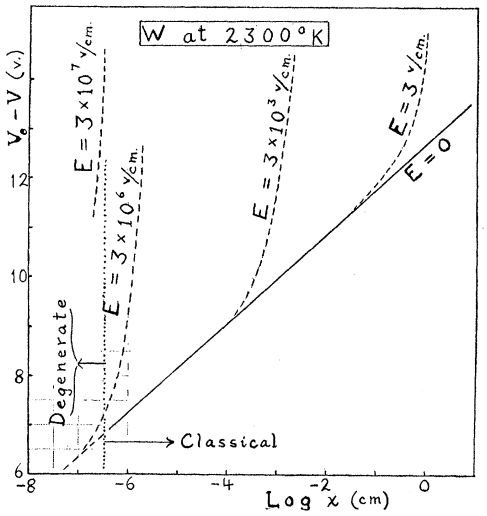

Fig. 1. Potential difference between conductor and points at distance x from surface.

Distribution of Electrons

The equilibrium distribution of electrons corresponding to this potential distribution, found by Eq. (1), is then given by

$$n = \frac{kT}{2\pi\epsilon^2 x^2}, \quad x \gg \frac{2kT}{\epsilon\beta} (\sim 10^{-10} \text{ cm}) \tag{10}$$

for zero applied field and for $x < x'$ for retarding fields.

For $x > x'$:

$$n = \frac{E^2}{2\pi kT} \cdot e^{-\epsilon E/kTx}. \tag{11}$$

It is seen that *the concentration of electrons at external points is independent of the nature of the emitting body*, and depends only upon the temperature, the distance from the surface, and the applied retarding field where effective,

i.e. outside the critical distance x'. This agrees with the result reached by Langmuir[8] for the completely classical case in the absence of applied field. Fig. 2 shows graphically the relation between n and x, covered by Eq. (9) and (10), the solid and broken lines having the same significance as before. The effect of an applied retarding field is to cut off the electron atmosphere quite sharply at the critical distance x', whereas inside the critical distance the density is not appreciably affected. For very high fields such as 10^6 v/cm, the electron atmosphere is effectively reduced to a layer about 10^{-6} cm in thickness within which the state is increasingly degenerate. Again attention may be called to the point that retarding fields of cold emission strength control the electron density down into the degenerate region.

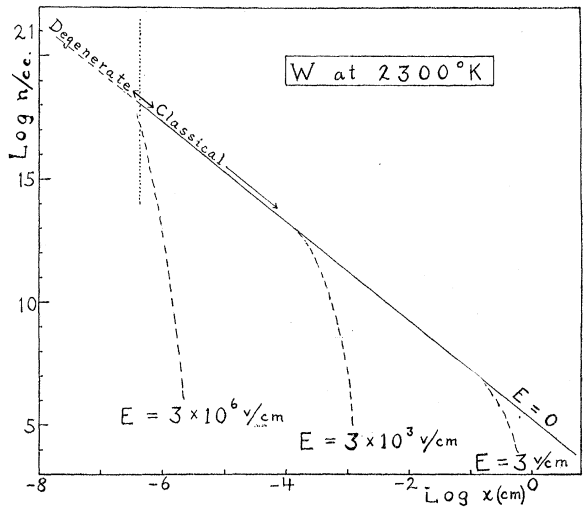

Fig. 2. Electron concentration vs. distance from surface.

The fact that the electron concentration is independent of the metal does not mean necessarily that according to this hypothesis all metals should yield the same thermionic currents in the absence of an applied field as the experiment would usually be performed. If the concentration given by Eq. (10) is used to derive the thermionic current density under these conditions, we have $I=(m/\epsilon)(kT/2\pi m)^{3/2}\ 1/x^2$. This would be the current density due to electrons striking an electrode at the distance x, assuming the current so small that equilibrium is maintained and assuming that the collecting electrode in no way affects the electron density or the potential distribution which would exist in its absence. At first sight it might appear that a suitable potential for this electrode could be computed by Eq. (7). Thus at a point 1 cm distant from a plane tungsten cathode at 2300°K the calculated potential is 12.7 v. with respect to the cathode. It does not follow directly however that the collecting anode will serve its purpose if set at this potential, since the anode, even though cold, has its own electron atmosphere and con-

[8] Langmuir, reference 3.

trols the potential in its neighborhood in a manner similar to the cathode. Clearly also any attempt to set the anode negative with respect to the cathode would put its own electron atmosphere under an accelerating field. It follows that, for a complete solution of the problem of thermionic currents between plane parallel electrodes from the present point of view, the electron atmosphere surrounding *both* electrodes should be taken into account, the one being subject to an accelerating field, the other to a retarding field.

A point of interest is that in equilibrium the electron concentration at any given distance from the surface is not so pronounced a function of temperature as one would judge from thermionic emission, since it is only directly proportional to the absolute temperature. Thus, on the hypothesis presented, a metal at room temperature should have an electron atmosphere whose density is of the order of one fifth to one seventh that at the same distance from the metal at thermionic temperatures. Over the same temperature range the equilibrium potential distribution is affected to a much less degree, by a factor of one-half to two-thirds at a distance of 1 cm, and and about five-sixths at 10^{-6} cm.

Although at the same temperature the electron density at a given distance from any plane metal surface should be the same (in equilibrium) in the absence of applied field, the potential should depend upon the nature of the metal. In fact the potentials at equal distances from two different metals at the same temperature should bear the ratio:

$$\frac{V_1}{V_2} = \frac{\log \beta_1}{\log \beta_2}.$$

If degeneracy is assumed within the metal $V_1/V_2 \sim \zeta_1/\zeta_2$ to a high degree of approximation and hence this ratio may differ from unity by a factor of two in extreme cases ($\zeta = (3n/4\pi G)^{2/3}h^2/2m$). Herein lies a possibility of a direct test as to the state of the electron gas within a metal, since if a classical state is assumed $\beta^2 = 8\pi n_0 kT$ where n_0 = electron concentration within the metal. Then, assuming the (classical) electron gas density within a metal proportional to the number of atoms *per cc.* V_1/V_2 would never differ from unity by more than about 5 percent. It may be possible to make this test by comparing the potentials required to produce equal currents from two different metals under otherwise identical conditions.[9]

The field intensity at external points in the absence of applied field, or within the critical distance x' with a retarding field is

$$\frac{dV}{dx} = -\frac{2kT}{\epsilon x} \tag{12}$$

The image force law gives an intensity $-\epsilon/4x^2$, and the ratio of the space charge intensity to the image force intensity is therefore $(dV/dx)_s : (dV/dx)_i = 8kTx/\epsilon^2$. At 300°K this ratio is $1.4\times10^6 x$; at 2300°K, $1.1\times10^7 x$. The two intensities are equal at $x = 7\times10^{-7}$ cm (300°K) and at $x = 9\times10^{-8}$ cm

[9] Cf. Bartlett and Waterman, reference 1.

(2300°K). Outside this distance the intensity reckoned on the space charge basis is greater than that due to the image force, increasingly so as the distance increases. Thus the former is 10^3 times the latter at a distance of 10^{-4} cm. Partial quantitative support for this conclusion is seen in experimental determinations by several investigators[10] of the field intensity close to a metal surface. In the most recent work Lawrence and Linford find the field intensity quite close to the surface (between 10^{-7} and 10^{-6} cm) to agree with the image force value, whereas at greater distances the intensity is consistently greater than that computed from the image force. This would be in general agreement with the present calculations.

Electron Separation Distance

Taking the mean distance between adjacent electrons as $n^{-1/3}$ this distance d compares with the distance x from the surface as follows:

$$\frac{d^3}{x^2} = \frac{2\pi\epsilon^2}{kT} = 4.5 \times 10^{-6} \text{ at } 2300°K.$$

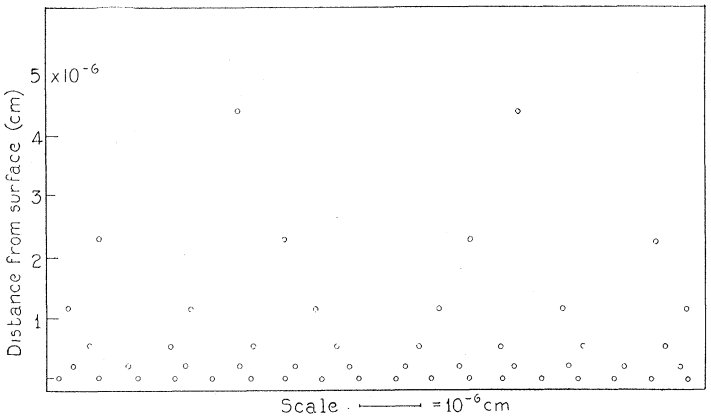

Fig. 3. Approximate indication of mean electron spacing.

Thus at 2300°K an electron 4.5×10^{-6} cm from the surface is at the same average distance from its neighbors. Closer to the surface it is farther from its neighbors than it is from the surface, and outside this distance the reverse is true. This calculation gives of course roughly the mean distance between electrons in a plane parallel to the surface and not in a direction perpendicular to this. Except at the closest distances an electron will always have a fairly dense atmosphere between it and the atoms of the metal. This is illustrated crudely by Fig. 3 where a rough picture is sketched in two dimensions to show the distribution of electrons between the surface and two electrons at the above distance of 4.5×10^{-6} cm. In this figure the horizontal distance between electrons has been computed from the above equa-

[10] Becker and Mueller, Phys. Rev. **31,** 431 (1928); Reynolds, Phys. Rev. **35,** 158 (1930); Lawrence and Linford, Phys. Rev. **36,** 482 (1930).

tion and the electrons are simply spaced symmetrically about a central vertical line. The range shown is that in which the image force action is utilized to explain the Schottky effect. The figure is illuminating in showing why according to the space charge analysis an image law may be used as an approximation *provided most electrons have been removed beyond a certain distance from the surface* (thus presumably for strong fields), though the plane to be used for image calculation would appear not to coincide with the surface atomic layer.

Space Charge vs. Image Force

The validity of space charge effects in the cases here treated (zero or retarding fields) is of course well known. The present analysis however brings out the fact that an applied retarding field has no appreciable influence on the potential or the electron density within a certain critical distance from the surface in question. This likewise appears to be not far from the truth for accelerating fields from Bartlett's calculations. That being the case a comparison of image force deductions with those of space charge inside this critical distance seems to be legitimate and desirable. When this is done the following conclusions may be drawn:

(1) The electric intensity due to space charge exceeds the image intensity at all distances from the surface beyond points so close that the surface structure should begin to play a part, where the two are equal. Experimental evidence on this point agrees better with the space charge intensity.

(2) The mean distance between adjacent electrons in a plane parallel to the surface is of the same order of magnitude as their distance from the surface, as calculated from space charge considerations. At the same time the calculation indicates the justification of an image force as an approximation, in the presence of strong fields.

Similar calculations based on the image law alone show it to be self-consistent, i.e. the mean distance between adjacent electrons is very much greater than the distance from the surface.

(3) The order of magnitude of the potential difference between the interior of the conductor and external points, as computed from space charge, is in agreement with the requirements of the Sommerfeld electron theory, thus giving directly the possibility of a work function of the correct magnitude. The value of the work function so obtained would depend upon the concentration of electrons available for thermionic emission ("thermelectrons"?) within the conductor, thus relating the work function with the thermodynamic potential.

The image force calculation of the work function can also be made consistent with the Sommerfeld theory by reducing (approximately by a factor of two) the distance from the surface at which the image law ceases.

The author is indebted to Professor R. S. Bartlett for many stimulating discussions, whose space charge analysis under accelerating fields was responsible for the present paper.