A Brief Primer on Thermionic Emission

Muhammad Nasim

Semester VI, B.Sc. Physics (Hons.)
Dept. of Physics, Scottish Church College
University of Calcutta, India.

Contents

1 A. Scope and objectives.

1.1 Definitions.

The emission of electrons across the boundary surface that separates a heated electronic conductor from an otherwise nonconducting space has become synonymous with the term "thermionic emission". The broadest application of the word thermionic might include the emission of charged atomic or molecular particles that may carry with them either a net positive or a net negative charge. Since these phenomena are so very different basically, this article will be devoted exclusively to the more fundamental aspects of the experimental and the theoretical investigations of the phenomenon of electron emission from heated conductors.

Thousands of experiments have been reported in the literature and serve as the basic work material from which an explanation of the phenomenon in terms of the fundamental principles of physics emerges. The studies relate to four surface classifications which are:

- clean homogeneous surfaces;

- clean heterogeneous surfaces;

- simple composite surfaces;

- complex surfaces.

To clarify these classifications an illustration of each will be given. Single crystal wires of circular cross section have been used as sources of thermionic electrons and provide the nearest approach to the realization of experimental conditions appropriate to theoretical interpretation.

Emission can be observed and investigated in detail from the more important crystallographically homogeneous surfaces. These surfaces must be maintained under such perfect vacuum conditions that an absolutely negligible fraction of a monomolecular layer of impurity is present. Since fundamental studies show that the thermionic emission is dependent not only on the atomic composition of the emitting conductor but also on the crystallographic structure of the exposed surfaces, it is evident that practically all investigations that describe the electron emission from polycrystalline substances yield data characteristic only of the particular specimen. In general such observations measure the electron emission summed over an assembly of *heterogeneous surfaces*, which can never be accurately described. Most of the work reported in the literature of the subject applies to these surfaces.

At a given temperature, the efficiency of electron emission from a given conductor may be altered through many orders of magnitude by the adsorption of polarizable atoms or molecules on an otherwise clean homogeneous or heterogeneous underlying conductor. The presence of a surface-layer coverage having a density even smaller than 1/100 part of a monolayer can be observed to alter the emission properties. Such surfaces are classified as *simple composite surfaces* if the extent of the coverage is of the order of a monolayer or less.

The last of the above four classifications, the *complex surface*, is by far the most important in terms of its usefulness as a source of electrons and includes as its most important member the *oxide cathode.* The structure represents an emitter which depends on the conduction of a heated metallic support such as nickel or platinum upon which has been placed, after due processing, a layer of alkaline earth oxide crystals. The surfaces of these crystals serve as the emitting areas. These crystals are generally solid solutions of barium oxide and strontium oxide of comparable proportions and sometimes have traces of other substances added. It is not unexpected that such a complex emitter will have properties very difficult to explain.

1.2 Theory and experiment.

It is an illusion to believe that the main features of thermionic emission have been worked out theoretically and are in agreement with experiment. In spite of the generality often associated with the thermodynamic interpretation of thermionic emission, emphasis must be given to the fact that this branch of theory cannot be relied upon to give accurate information concerning the current flow across a boundary under experimental conditions that violate the basic assumptions of the theory. The most important assumption made is that the system under consideration can be bounded in a manner that will still permit the actual measurement of an electron emission across a boundary. Thermodynamic considerations can be applied to the electron gas in the interior of a single crystal of conducting substance so cut out as to bound the interior cavity by surfaces of perfect homogeneity as regards their crystal structure. With the combined help of the equations of thermodynamics and electrostatics the time average of the density of electrons can be specified as a function of the coordinates within the cavity. The pressure that these electrons would exert on the surface of the cavity can be computed with confidence and from these quantities one might presume to calculate a current of electrons which would flow from the interior of the conducting specimen across a surface boundary to the region just outside the conductor. To assume that such a calculation of the current would be directly related to an observable emission current is wrong. No theory as general as this can predict the fraction of the electrons which are reflected at the boundary.

Even though usually considered to be less general, the statistical theory of an assembly of free electrons is more capable of giving valid information concerning the thermionic emission process. It will therfore be appropriate to base practically all of the theoretical analysis brought forward in this chapter on the application of the statistics of free electrons to thermionic emission phenomena.

2 B. Historical highlights.

2.1 Introduction.

It will be the purpose of this section to review briefly some of the main events that have marked both the development of the theory and the understanding of thermionic emission as well as the technological advances which have been made during the past 70 years.

Following this qualitative review of events a detailed analysis will be given to review the present state of our understanding with respect both to theory and experiment.

2.2 Discovery and identification of thermionic emission.

That negative electricity escapes from hot filaments was probably first established by THOMAS A. EDISON and later identified by WILLIAM H. PREECE as the "EDISON Effect". The account by PREECE of his own experiments on the EDISON effect does not separate the phenomenon now recognized as thermionic emission from the "blue effect" which was evidently the ionization of the residual gas produced by the electrons as they were accelerated from the negative hot filament to the plate of the diode. The identification of the charge carrier emitted from the hot carbon filament as a particle with a very small mass compared with that of a hydrogen ion and with a charge equal in magnitude but opposite in sign to that of the hydrogen ion was made by J. J. THOMSON. In spite of the important experiments of J. J. THOMSON, general agreement that electron flow through conductors and electron emission from hot surfaces are truly different phenomena from ionic flow through substances and ionic conduction through gases did not come until about 1914.

2.3 RICHARDSON equations.

Thermionic emission is so intimately associated with the phenomenon of electronic conduction in solids that advances in these two fields of scientific investigation are associated. The DRUDE development of the theory of free electrons in metallic conductors paved the way for the better understanding of thermionic emission which marked the contributions of. W. RICHARDSON. The basic idea of work-function as being a measure of the energy per electron required to transfer charges from the interior of the conductor to the field-free space outside of it is largely due to RICHARDSON. Founded on a very literal classical interpretation of the free electron theory of electronic conduction in metals, RICHARDSON derived his first thermionic emission equation which took the following form:

$$I = ne(\frac{k}{2\pi m})^{\frac{1}{2}}T^{\frac{1}{2}}e^{\frac{-e\phi}{kT}} \tag{2.1}$$

The recognition of difficulties encountered by the classical free electron theory of conduction and its relation to the specific heat of metals led RICHARDSON and VON LAUE to the "T^2" equation given as follows:

$$I = AT^2 e^{\frac{-e\phi}{kT}} \tag{2.2}$$

In its original form this equation depended upon thermodynamic arguments and at the present time it is accepted as the correct expression for electron current flow at a boundary which is in a system maintained under conditions of thermodynamic equilibrium. The mistake generally made in the application of this equation is that the current I is identified as the thermionic emission current one should expect to observe in a laboratory experiment. The current density of Eq.(2.1) is independent of reflection and of other phenomena that may alter the distribution in energy of the electrons which do cross the boundary in an

actual emission experiment. A second common error in the application of Eq.(2.2) to thermionic emission is the assumption that the true work-function ϕ is a constant.

2.4 CHILD-LANGMUIR space charge.

A second effect produced by accelerating fields-an important one in the understanding of thermionic emission-was recognized by LANGMUIR and CHILD and others as being accounted for by the phenomenon of space charge.

As the temperature of an emitting conductor increases, the observed current does not increase indefinitely, even though a fixed strongly accelerating positive potential is maintained on the electron collector. If the number of electrons in transit between the emitter and the collector exactly equals the total surface charge maintained on the collector by the external circuit, then the electric field at the emitter becomes zero. Further increases in temperature are followed by very little increase in observed current because of the development of a retarding field at the surface of the emitter produced by space-charge. Even though space-charge effects are strongly dependent on electrode geometry and act in the space well outside of the thermionic emitter itself, it is necessary to have a full understanding of their influence. Thermionic emission is an electron flow observed as a current between suitably placed electrodes and the phenomenon of space charge seldom should be neglected in the interpretation of the observations

3   C. Theory.

3.1   Free electrons.

The basic concepts needed for the derivation of thermionic emission equations are very elementary and yet they are sufficient for the purpose. One pictures the interior of a conducting crystal as an organized arrangement of atoms characterized by specific interatomic distances which are specifically dependent on the atomic composition and the phase taken on by the crystal, depending upon the temperature and the previous temperature history of the specimen. Each crystal as a whole should be thought of as being electrically neutral within any extended region in the interior. Any excess of charge either positive or negative will be found at the surface only. Quantum theory indicates that most of the electrons that neutralize the positive charge on the atomic nuclei are localized near them and in general contribute nothing to the electrical conductivity of the specimen. The valence electrons associated with these atoms, however, occupy quantum states that extend throughout the entire interior of each isolated crystal and it is to these electrons that the statistical theory of the free electron gas may be applied. The free electron theory as applied to these valence electrons describes their behavior in practically classical terms and finally depends upon experiment to justify the applicability of the simplifying assumptions. It is the purpose of this article to indicate as clearly as possible that the most recent experiments serve to support strongly the concepts of the mechanism of thermionic emission which can be derived from the theory even though they are based on a semiclassical analysis of behavior of valence electrons in a conductor.

3.2 Three basic assumptions.

The first assumption made for the development of this theory is that the inter-electronic forces can be neglected and therefore the electrons behave as though they were particles of three degrees of freedom. The phase space suitable for representing the behavior of an assembly of electrons can therefore be taken to be a six-dimensional phase space in which a representative point exists for each electron in the assembly. The six bits of information needed to localize this representative point are three coordinates and three components of momentum. The second assumption is that for each quantum state an extension in phase space of size h^3 is needed and that a representative point cannot be localized (nor need it be) more specifically than to indicate that one representative point lies within the quantum-state region. Actually this is not quite the whole story because quantum principles permit two electrons to occupy a single quantum state if their spin vectors are always antiparallel. A factor 2 that appears repeatedly in the equations derived on these assumptions is therefore this weight factor which is thus incorporated into the theory. Already the third postulate has been mentioned, namely, the PAULI Exclusion Principle, which limits the number of electrons in a given quantum state to two with antiparallel spin vectors.

It is the purpose of a statistical theory to find an expression for the distribution of representative points in phase space which is consistent with basic principles of thermodynamics and has associated with it the greatest likelihood of occurrence. The function thus obtained, without the need for introducing any additional assumptions, is the following:

$$f(\epsilon) \; dx \; dy \; dz \; dp_x \; dp_y \; dp_z = 2 \frac{dx \; dy \; dz \; dp_x \; dp_y \; dp_z}{h^3} [\frac{1}{e^{\frac{\epsilon - \mu}{kt}} + 1}] \qquad (3.1)$$

Some explanation of this equation may make its use and meaning easier to grasp. The energy is generally separable into two terms, one of which expresses the kinetic energy of a particle whose representative point lies in a specified region in phase space, and the other term is the potential energy expressible in terms of the coordinates of a particle whose representative point is in that region in phase space. The quantity μ is a constant for a given problem which contains implicitly the concentration of electrons and is a function of the temperature. The fundamental concept that determines the value of this parameter is that the integration of Eq.(3.1) over the entire phase space shall exactly equal the number of electrons in the assembly, that is, the number of free electrons within a crystal, for example. Although this statement defines the manner in which the constant μ is determined, there is a second meaning to the constant which is interesting to note, if it applies to a concentration of electrons of the order of 10^{20} per cm^3. The energy value μ is that to be associated with that quantum state for which the probability of occupancy is exactly one-half.

For electron concentrations less than approximately 10^{19} per cm^3 the appropriate value of μ is generally a negative number. This statement demands a word of explanation. The simplest application of Eq.(3.1) is made to regions in coordinate space over which there is no change in potential energy. It is therefore sufficient for the present purpose to apply Eq.(3.1) to problems in which the potential energy may be taken to be zero. In that case the energy ϵ will be the kinetic energy of the electron whose representative point lies in

a particular region of phase space. In problems of this kind which occur in connection with the theory of the oxide cathode, the algebraic sign of the quantity μ can be defined as negative, and therefore, it lies below the conduction band in the energy, band system. All of the available quantum states associated with the particular problem for low-density distributions of the electrons are less than half filled if μ is negative.

Note that the extension in phase space $2\frac{dx\ dy\ dz\ dp_x\ dp_y\ dp_z}{h^3}$ represents the number of quantum states in this extension, since the extension per quantum state is h^3 , as mentioned previously. The factor 2 is the double occupancy of a quantum state by the two electrons with antiparallel spin vectors.

Finally, the factor in the square brackets of Eq.(3.1) can be identified by its name the "FERMI factor" which gives a direct means of computing the probability that a given quantum state identified by its energy e will be occupied. The energy is given explicitly in terms of the momenta and the coordinate values associated with the representative point in phase space. The name given to the quantity μ is the "FERMI level". It is evident at once that if the numerical value of μ is positive, then there can be an energy level ϵ exactly equal to μ and, as mentioned above, the FERMI factor takes on the value $\frac{1}{2}$.

3.3 The electron flow equation.

Although Eq.(3.1) is the basic starting point for all equations relevant to thermionic emission, the following equation which is derived directly from Eq.(3.1) without the introduction of any approximations is the most important equation applicable to thermionic emission.

$$N(\epsilon_x)d\epsilon_x = 2\frac{2\pi mkT}{h^3}ln(1 + e^{-\frac{\epsilon_x-\mu}{kT}})d\epsilon_x \tag{3.2}$$

The independent variable in this equation ϵ_x is defined by

$$\epsilon_x = \frac{p_x^2}{2m} \tag{3.3}$$

By the use of Eq.(3.2), the number of electrons $N(\epsilon_x)d\epsilon_x$ that cross a unit area in unit time with kinetic energy associated with the positive x direction of motion can be computed for the energy range, $d\epsilon_x$. This equation holds for all values of μ, either positive or negative, and therefore applies to all densities of electrons provided μ is expressed relative to the energy level for which the kinetic energy is zero or, in other words, with respect to the potential energy at the region in space for which the number of electrons crossing a boundary perpendicular to the x direction is being computed. The first application of this formula will be to compute the "random" currents which impinge on various boundaries of a pillbox-like cavity within the interior of a homogeneous crystal.

3.4 Electrons in a cavity.

The pillbox problem is of interest because it is the only example of the application of theory to an experimentally realizable structure for which all of the essential details are easy to describe. The structure visualized is shown in Fig. 1. The cross-hatched solid structure S represents a section through the interior of a single crystal and the cavity within this crystal is represented by C.

The perpendicular distance across that cavity, a, b, should be visualized as being not less than $10^{-4}cm$. and can very well be any amount larger than this. The requirement that the cavity be essentially pillbox form is necessary because of the need to have the entire interior of the cavity of a single surface structure type. The pillbox has the further advantage that the problem can be handled exactly, even though sufficient electrons exist in the cavity to give an appreciable space-charge field there. The first steps of the discussion can be carried through without the introduction of space charge as a factor of any importance.

In the energy diagram of Fig. 2 the potential' energy of an electron is shown as a function of distance as one progresses in the x direction from A to B. The region A to a, is the potential in the interior of the solid taken here to be uniform. It will be shown later that the periodicity of the true potential is of no consequence in the thermionic emission theory. The potential of the electron in the space between a and b is shown to be higher than that in the interior of the metal by an amount W_a. This energy difference is the integration of all of the actual forces that act on an electron as it escapes from the metal into the cavity. In the absence of space charge the cavity potential will be constant at distances greater than approximately 10^{-5} cm. from either surface, since the dominant long-range force acting on an electron is the mirror-image force which at this distance has fallen to a negligible amount. Eq.(3.2) may be used to calculate the number of electrons which approach the boundary from the left at a, with energy between ϵ_x and $\epsilon_x + d\epsilon_x$ associated with the x component of the momentum. In the space between a and b the corresponding energy state lies at ϵ_x'.

For the net current to be zero it is necessary that the current in this band from the left be equal and opposite to the current in the band which approaches surface a from the right. This statement would in general not be true if it were applied to a geometrical configuration in which currents were being observed as electron emission currents in the usual way. An essential part of this analysis is that the entire region surrounding the cavity be at a constant temperature and of course this includes the cavity itself.

In the interior of the crystal the FERMI level, FL, is located at an energy μ_s positive with respect to the potential energy line Aa relative to which the kinetic energy ϵ_x, is referred. The application of Eq.(3.2) shows that there is a simple and yet a necessary condition which must be satisfied if the cavity currents are in statistical equilibrium with the currents flowing in the solid. This condition is that the FERMI level be continuous right through the cavity space. Relative to the potential energy of an electron in the cavity, the FERMI level is negative, the amount shown as μ_c. The formal writing of the two equations for the two electron streams serves to illustrate this point and will be used for further development. These equations are the following:

$$N_{xs}d\epsilon_x = 2\frac{2\pi mkT}{h^3}ln(1 + e^{-\frac{\epsilon_x - \mu_s}{kT}})d\epsilon_x \qquad (3.4)$$

$$N_{xc}d\epsilon_x = 2\frac{2\pi mkT}{h^3}ln(1 + e^{-\frac{\epsilon_x' - \mu_c}{kT}})d\epsilon_x \qquad (3.5)$$

It is clear from an inspection of these two equations that the necessary condition for

the equality of these two flows of electrons is that the exponents be equal and the following equation may therefore be written:

$$\epsilon_x - \mu_s = \epsilon_x' - \mu_c \tag{3.6}$$

Eq. (3.7) gives additional relations as a result of the reorganization of Eq. (3.6) which are self-evident:

$$\epsilon_x - \mu_s = \epsilon_x' - \mu_c = W_a \tag{3.7}$$

The final rearrangement of this equation is written as follows:

$$-\mu_c = W_a - \mu_s = (true \ \ workfunction) \times e = \phi e \tag{3.8}$$

This equation stated in words demonstrates the fact that the true work-function expressed in energy units is a direct measure of the location of the FERMI level appropriate to the cavity space outside of a thermionic emitting conductor *when equilibrium exists between the conductor and the space.*

3.5   The RICHARDSON equation.

The integration of Eq.(3.4) between the limits of $\epsilon_x = W_a$ and ∞ gives a means of calculating the total electron current that impinges on the boundary at a from the interior with the energy range limited, in such a way that any of the electrons included could have gone into the space if reflection effects at the boundary a did not exist. This result is given as Eq. (3.9). The integration of Eq. (3.5) gives the total current which would flow into the conductor from the exterior under conditions of perfect equilibrium. These two currents must be equal. These equations integrated give the following results:

$$I_s = \frac{2e(2\pi mkT)kT}{h^3} e^{-\frac{W_a - \mu_s}{kT}} \tag{3.9}$$

$$I_c = \frac{2e(2\pi mkT)kT}{h^3} e^{-\frac{\mu_c}{kT}} \tag{3.10}$$

The validity of Eq.(3.10) depends on the assumption that the numerical value of μ_c is not less than 5 kT for an accuracy of better than 1%. For smaller values of μ_c, other terms in the power series expansion must be used.

The fact that μ_c, is clearly a negative number implies that the electron density in the cavity space is smaller than approximately 10^{19} per cm^3 . Under these conditions the statistical theory gives a suitable expression for μ_c which is the following:

$$\mu_c = -kTln[\frac{2(2\pi mkT)^{\frac{3}{2}}}{n_c h^3}] \tag{3.11}$$

The substitution of this value for μ_c, into Eq.(3.10) yields the following:

$$I_c = n_c e(\frac{kT}{2\pi m})^{\frac{1}{2}} \tag{3.12}$$

in which n_c is the concentration of electrons in the cavity space near enough to the surface so that space-charge fields can be neglected and yet far enough from the surface so that the mirror-image fields are negligible. This equation is the familiar one from classical mechanics and may be explained in the following terms: $(n_c/2)$ represents the concentration of electrons moving with a component of velocity in any specified direction; $2(kT/2\pi m)^{1/2}$ represents the average of the velocity component of these electrons in a classical distribution; and e is the charge on an electron.

The rewriting of Eq.(3.9) yields at once the RICHARDSON form of the equation so often misused when it is identified with observable thermionic emission.

$$I_s = \frac{4\pi mk^2 e}{h^3} T^2 e^{-\frac{W_a - \mu_s}{kT}} \tag{3.13}$$

The first factor of this equation may be recognized as the familiar universal thermionic constant A.

$$A = \frac{4\pi mk^2 e}{h^3} = 120 \quad amp/cm^2 \; T^2 \tag{3.14}$$