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by

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### Introduction

Textbook writers<sup>1</sup> who set for themselves the problem of discussing potential as it applies to electrical problems usually encounter difficulties if they ignore the basic concepts put forward by Langmuir<sup>2</sup> when he coined the work "motive" and defined its principal use. His definition is: "The motive is best defined as a scalar quantity whose gradient in any direction and at any point represents the force component per unit charge which must be applied to an electron or an ion to hold it in equilibrium at the given point." The gradient of the motive is the "motive intensity," and it is therefore a vector which measures the force per unit charge on an electron at the point in space at which the gradient is taken.

It is to be noted that this definition differs from that of "electrostatic potential" and of "electric intensity" in that definitions for them are given as the limit of the time average of the work or force respectively per unit charge as the charge approaches zero.

### Sect. 1 Definitions

The principal use that is made of motive functions is that associated with potential energy distributions in space which are either invariant with the time or else change so slowly that the transit time of the electrons or ions can be neglected. Such a system is classified as a "conservative system" in that the total energy of an ion or electron can be considered as the sum of its kinetic energy and its potential energy. Except insofar as the particular electron or ion receives or delivers energy to or from other bodies including light quanta its total energy remains constant. Thus in the passage of an electron across a material boundary it is the motive function and not the electrostatic potential which establishes the potential energy of the electron and where this changes, the compensating change in kinetic energy takes place to hold its total energy constant.

The similarities and the differences between electrostatic potential and motive can be made more explicit with the help of defining equations. The first of these applies to electric intensity and is written as

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$$\left( \frac{\vec{F}}{4\pi\epsilon_0 q} \right)_{\lim q \rightarrow 0} = \vec{E} \quad | \quad 1:1$$

The electric intensity vector  $\vec{E}$  is thus defined as the limit of the force per unit charge which acts on a charge  $q$  as the magnitude of the charge approaches zero. The units used here give the electric intensity in volts per meter with the force expressed in newtons and the charge  $q$  in coulombs. The permittivity of free space is  $\epsilon_0$ .

The basic difference between the motive intensity and the electrostatic intensity is best illustrated by the equation

$$\left( \frac{\vec{F}}{4\pi\epsilon_0 q} \right)_{q=q} = \vec{I}_M \quad | \quad 1:2$$

Here again the vector force that acts on a charge  $q$  is related to the motive intensity by an equation which is completely analogous to Eq. 1:1 except in that the motive intensity is the force per unit charge when the charge is that existing at the point in question. An electron or an ion can be thought of as being acted upon by an electrostatic field produced by a distribution of charges so far away from the point in question that the defining charge  $q$  does not disturb the distribution of the charges that create the field sufficiently to make a distinguishable difference between the electrostatic intensity and the motive intensity. If the ion or electron is in the immediate neighborhood of matter such as atoms, molecules, material surfaces such as metals, semiconductors and insulators, they create polarizations or redistributions of charge which result in forces generally proportional to the charge itself and inversely related to the distance between the electron or ion and the material inhomogeneity. Clearly, the motive intensity can include "mirror-image forces" which play the dominating part in the motive function as an electron either approaches a conducting surface or leaves it while some electron emission phenomenon is being examined such as the thermionic emission of electrons, the photoelectric emission of electrons, or even the field emission of electrons. Not only are electrons acted upon by these forces, but also ions are accelerated toward surfaces if they are free to move as a result of induced charge distributions which are completely absent when the electric intensity at the point in question is defined as in Eq. 1:1. The distribution of motive intensity in space as defined by Eq. 1:2 is an operational one broad enough to include the induced effects.

The general concept of "potential energy" in a conservative field implies that energy is required or delivered to transfer an object, such as an electron, from one point in space to another. A difference in potential or a difference in motive is readily defined. There is no absolute value of either these scalar quantities except in the sense that some arbitrarily chosen region in space can be declared to be at the reference potential relative to which all other potentials or motives pertinent to the problem can be evaluated. The two equations used to define a difference in electrostatic potential and a difference in motive are given as:

$$V_a - V_b = \int_a^b \vec{E} \cdot d\vec{r} = \left[ \int_a^b \left( \frac{\vec{F}}{q} \right) \cdot d\vec{r} \right]_{\lim q \rightarrow 0} \quad | \quad 1:3$$

$$M_a - M_b = \int_a^b \vec{I}_M \cdot d\vec{r} = \left[ \int_a^b \left( \frac{\vec{F}}{q} \right) \cdot d\vec{r} \right]_{q=q} \quad | \quad 1:4$$

Since Eq. 1:3 gives the line integral of the force per unit charge as the charge approaches zero, forces which depend on the charge itself such as mirror-image forces can contribute nothing to the difference in the electrostatic potential between the space point a and space point b joined together by a line in an electrostatic field. Since the difference in motive depends on the line integral of the force function that actually applies when the charge is that of the electron or ion, the change in the motive at b relative to that at a is the useful quantity which can include charge displacements that take place as the charge q moves from position a to position b.

The differential forms of Eqs. 1:3 and 1:4 may be written:

$$\vec{E} = -\nabla V \quad | \quad 1:5$$

$$\vec{I}_M = -\nabla M \quad | \quad 1:6$$

Here the electric intensity is expressed as the negative of the gradient of the electrostatic potential and the motive intensity is expressed in a like manner as the negative of the gradient of the motive. The application of Gauss' law to Eq. 1:5 yields Poisson's equation which is

$$\nabla^2 V = -\frac{\rho}{\epsilon_0} \quad | \quad 1:7$$

This equation is applicable only in regions of space sufficiently far away from material boundaries so that the electron or ion itself does not disturb the average electrostatic potential as it does when the electron or ion approaches a material boundary. There is no meaning to the corresponding equation for  $\nabla^2 M$  except in regions far from material boundaries. When space charge is present at a sufficient density to give an electrostatic intensity comparable with the mirror-image force at the point in space, then a superposition of the two may be used.

### Sect. 2 Mirror-Image Forces Considered Quantitatively

Consider, for the purposes of calculation, that an electron is approaching the face of a relatively large single crystal of a conductor positively charged to an amount equal to that of a single electron. It is necessary also to specify that the single crystal be constructed so as to exhibit a single crystallographic orientation. Thus a tungsten crystal in the form of a dodecahedron could be made to exhibit only surfaces which have normals in the (110) direction. For comparison, the (100) direction could be chosen and a cube would be the idealized shape of this crystal. These restrictions are placed in order to avoid the presence of local electrostatic fields which would otherwise be present due to equal and opposite surface charges that would result from the presence of surfaces of unequal work-function.

Depending on the size of the crystal, there will be a distance such that the induced surface charge of opposite polarity will result in a force of attraction acting on the electron which can be made vanishingly small and yet not precisely zero. An electron released with essentially zero kinetic energy at this point will be acted upon by this force and accelerated toward the surface over which an equal and opposite surface charge has been induced. As the electron approaches the surface, the force increases and the electron velocity toward the surface increases in such a manner as to keep the total energy of the electron constant. This force is measured as the motive intensity and the line integral of the motive intensity from the starting point to any point on the trajectory represents the change in motive and is a direct measure of the increase in kinetic energy. At distances larger than 4 or 5 times the interatomic spacing of the atoms in the conducting surface, the force function is independent of the exact nature of the conducting surface provided the restrictions mentioned above are satisfied. This force function is given by:

$$F_m = I_M q = \frac{q^2}{4\pi\epsilon_0 (2x)^2} \text{ newtons} \quad | \quad 2:1$$

In this expression,  $x$  is the distance in meters from a fictitious surface just inside of the real surface. The real surface may be defined as that surface perpendicular to the direction identified as the  $x$  direction and containing the time average location of the nuclei of the last exposed layer of atoms of the idealized crystal. If Eq. 2:1 is integrated to obtain the change in motive as the electron moves toward the surface from a very great distance to a specific location  $x$ , some 4 or 5 interatomic distances away or more from the real surface, the result is given by

$$M_x - M_\infty = \frac{q}{16\pi\epsilon_0 x} = \frac{3.6 \times 10^{-10}}{x} \quad | \quad 2:2$$

The insertion of suitable units in Eq. 2:2 gives the change in motive in volts. This is the convenient unit in electronics which when multiplied by the charge  $q$  expressed in coulombs gives the change in potential energy expressed in joules. Equation 2:1 shows that the mirror-image force function approaches infinity as the distance  $x$  from the fictitious surface approaches zero. In like manner, the change in motive as given by Eq. 2:2 also goes to infinity at zero distance.

Perhaps one of the most significant experimental demonstrations that the motive function changes by a finite quantity as the electron is accelerated by the mirror-image force finally to enter into the interior of a conducting surface depends on the experiment of Davison and Germer.<sup>3</sup> Briefly, their experiment involved the delivery of electrons to a single-crystal nickel surface at normal incidence. These electrons were launched by an electron gun at various electron energy values between 64 volts and 586 volts. A small number of the electrons interacted with the atoms of the crystal lattice to become refracted as electron waves and subsequently were re-emitted, with no loss in energy, in specific directions depending on the wavelengths associated with the electrons and the space distribution of periodic motive function within the crystal. The table of values computed by Hartree and published by Fowler<sup>4</sup> shows that for the 6 different launching energies used by Davison and Germer, the augmented energy which had to be added to the launching energy in order to establish agreement between theory and experiment for the refraction coefficient was 18 electron volts. Although Fowler considered this change in motive from the exterior to the interior of the

nickel crystal a reasonable value for nickel, it could very well have been slightly high unless consideration was given to experimental details which would require the removal of a surface layer of oxygen impurities and a correction for the actual work-function of the emitter used. These corrections should not be more than 2 or 3 volts. Therefore, to attribute as much as 15 volts to the change in motive for the nickel surface is firmly established by these experiments.

Although the interior of a metallic conductor such as tungsten must be thought of as a region of constant average motive, even though it will have a periodic character, the change in motive between the interior and the exterior will depend on the crystal structure of the surface that bounds the crystal. For the tungsten crystal, cut as a dodecahedron and exposing only (110) surface, the change in motive is likely to be close to 13 volts; whereas the tungsten crystal cut to expose only (100) surface will have a change in motive close to 12 volts. A single crystal of tungsten which has both of these surfaces exposed will have electrostatic fields of easily measurable magnitude out to distances away from the crystal comparable with the linear dimensions of the surfaces involved as a result of the local distribution of surface charge. The total amount of negative charge is exactly equal to the total positive charge if the crystal as a whole is electrically neutral. As a result of these local fields the change in motive from the crystal interior to a point far away from this isolated crystal will fall between 12 and 13 volts depending on the relative proportions of (110) and (100) surfaces exposed.

The main purpose of this discussion is to indicate that an electron upon approaching a surface is acted upon by the mirror-image force until it is within a few atomic distances ( $10^{-9}$  m). Between that point and the interior of the metal the actual motive intensity is weaker than the mirror-image intensity. The rougher the surface atomically speaking, the weaker the force. The adsorption of polarizable atoms such as cesium or thorium on tungsten contributes also to a significant alteration of the integral of the motive intensity because of the presence of strong localized electrostatic fields which are present. The integrated change in the motive due to an adsorbed polarized layer of atoms is generally expressible in terms of the average dipole moment per unit area of the adsorbed film. Depending on the direction of polarization, an adsorbed film can either reduce or increase the step in the motive function from the interior of a conductor to the region well outside of it.



Sect. 3. The Fermi Level and Its Relation to Fermi Energy

The problem that describes the motive function that connects the interior of a conducting crystal with an isothermal cavity with dimensions large compared with atomic dimensions is the only electronics problem involving motive changes that can be discussed rigorously. For the purposes of this discussion imagine two slabs of crystalline conducting material such as tungsten large enough so that a cavity can be cut in each one to a depth of approximately  $5 \times 10^{-5}$  m and with lateral dimensions over the surface of  $10^{-2}$  m by  $10^{-2}$  m. If the (100) direction is chosen to be perpendicular to the cavity surface, then the cavity can be rectangular and no surface will be exposed except the (100) surface. The two slabs of tungsten may be placed together to form in this manner a cavity  $10^{-4}$  m across with cross-sectional dimensions 100 times greater than this. The purpose in being this detailed with regard to the description of the cavity is that the analysis can best be carried through on a "one-dimensional" basis as we deal with the change in motive from the interior of the conducting crystal through the cavity at its center and back into the conducting material. An imaginary closed boundary surface can now be drawn through the crystal body itself and completely surround the cavity. Within this imaginary boundary the net charge must remain continuously zero at all temperatures. Although the analysis can be applied even though the cavity might contain ionizable gas such as cesium<sup>5</sup>, it will simplify the discussion to assume that the temperature range will not be so excessive that an appreciable number of positive ions in comparison with the number of electrons will be found in the cavity space. It is also assumed that the concentration of neutral atoms in the cavity space will be sufficiently small so that the electron flow will be governed entirely by the combination of mirror-image forces and electrostatic forces which in turn depend on there being a uniform distribution of positive charge over the interior of the cavity precisely equal to the total space charge of electrons within the cavity. Thus, the discussion will not be limited to a treatment of the problem in the absence of space charge, but full consideration will be given to its influence.

Crystals formed of materials that are found to be good conductors of electricity generally correspond to elements that have one or two electrons in the outermost quantum states of the atom. Upon the formation of a crystal, the actual physical space surrounding the nucleus of an individual atom, needed to accommodate one or more of these valence electrons is so large that when the atoms are brought together to form the crystal, the "overlap" of the space needed for these electrons is so severe that individual electrons are no longer associated specifically with individual atom cores, but fill in quantum states related to the crystal as a whole as though it were a gigantic molecule. This "molecule" must have quantum states both occupied and unoccupied available to the electrons in excess of the total number of these "free" electrons which were originally the valence electrons of the crystal's atoms. The distinction between the free electrons and the bound electrons is that the former are free to circulate throughout the entire crystal and respond to a very small motive gradient to give good electrical conduction. They must be considered to be in a state of motion even at the absolute zero of temperature. The bound electrons do not contribute appreciably to the electrical conductivity since their quantum states do not have available empty states associated with a small increase in kinetic energy. Exceptions occur as for example in silicon if there is a distribution of impurity atoms such as aluminum or boron present that can accept electrons as the temperature is increased and provide some empty levels inter-mixed with the higher of the filled levels.

Under isothermal conditions, and no externally applied potential differences, the net current across any boundary within the conductor averages to zero because the total random current in any particular direction is exactly offset by the corresponding random current in the opposite direction. An electron in motion has associated with it kinetic energy. As was indicated by the Davison and Germer experiment, the increase in kinetic energy as an electron traverses an external boundary with no loss in energy into the lattice, is a direct measure of the total change in the motive of a free electron as it enters the metal. As it traversed the space across the surface boundary to occupy a quantum state within the crystal, there was no change in total energy. The vast majority of electrons that are delivered to a surface in this manner from an external source lose energy rapidly soon after they enter the crystal because they at first occupy quantum states which under the conditions of the experiment would not normally be occupied. The fact that some electrons in the Davison and Germer experiment were refracted under the influence

of the periodic variation in the motive within the crystal and yet lost no energy indicates that for most purposes the location of the average value of the motive within the crystal compared with its average value outside of the crystal is a measure of the average kinetic energy associated with that quantum level within the crystal.

The occupation of available quantum states within a crystal which is very large compared with atomic dimensions is governed by Fermi statistics. Associated with each quantum state is an extension in space to be multiplied by a range in associated momenta such that the product of these two is  $h^3$ .

$$\left[ (\text{coordinate range}) \times (\text{momentum range}) \right]^3 = h^3$$

Each of the quantum states of a free electron described in this manner accommodates only two electrons of opposite spin. It follows, therefore, that, if the coordinate space available to accommodate a very large number of electrons is limited then a correspondingly wide band of energies must be included to provide the required number of quantum states to provide for the high density of freed valence electrons.

The occupancy of the quantum states by electrons can be discussed in the language of statistical mechanics. In this analysis, an "undetermined multiplier" may be introduced to assist in the discovery of that distribution of the electrons to the quantum states that corresponds to thermodynamic equilibrium at any particular temperature for any specified number of electrons moving in completely random motion within a space of constant average potential or motive. In order to determine the value of this multiplier, the sum of all of the occupied quantum states (including two electrons in each) must add up to be equal to the total number of free electrons within the space. In principle, there is no difference in the way of computing this multiplier dependent both on the temperature and the density of the electrons. However, arithmetical convenience necessitates the use of two different formulas depending on whether the concentration of electrons is higher than  $10^{27}$  electrons per cubic meter or less than  $10^{24}$  electrons per cubic meter. For the intermediate densities between these limits, numerical evaluation is quite possible by means of formulas containing more terms than are needed for the extremes. In general, the undetermined multiplier is best expressed in an exponential form by

$$A = e^{\frac{\epsilon_F}{kT}} \quad | \quad 3:1$$

In this equation,  $A$  is a pure number, being the undetermined multiplier mentioned above, applicable to a particular problem of a specified density of electrons in a field-free space at a temperature  $T$ . The product  $(kT)$  is an energy expressible in joules. There is, therefore, a corresponding energy also expressed in joules of  $\epsilon_F$  which when inserted into Eq. 3:1 gives the required value of the undetermined multiplier  $A$ . Having defined this energy by means of Eq. 3:1, no statement has been made which limits its value to positive numbers only. Large values of  $A$  obviously call for a positive number for  $\epsilon_F$ , whereas small values of  $A$  which may be considerably less than unity, call for negative values of  $\epsilon_F$ .

The culmination of this statistical approach is the Fermi factor given as follows:

$$\text{Fermi Factor} = \frac{1}{e^{\frac{\epsilon_i - \epsilon_F}{kT}} + 1} \quad | \quad 3:2$$

This factor is also a pure number and is a direct measure of the probability that the  $i^{\text{th}}$  quantum state which has associated with it the total energy  $\epsilon_i$  will be occupied. This energy must be related to the same frame of reference as that which determines the numerical value of the Fermi energy  $\epsilon_F$ . Thus, if  $\epsilon_i$  is the kinetic energy associated with an electron within the interior of a conductor of uniform average potential, then the energy  $\epsilon_F$  must be measured from the same reference which is the average motive within the interior of the crystal. It follows from this definition that in any solid in which there is a quantum state at the energy level  $\epsilon_i$  equal in value to the energy  $\epsilon_F$  established basically by Eq. 3:1, the probability that this quantum state will be occupied is  $(1/2)$ . All quantum states of lesser energy will have an expectancy of occupation which approaches unity very rapidly as this energy difference increases. If the quantum energy exceeds  $\epsilon_F$  the probability of occupancy falls very rapidly and approaches zero.

If  $\epsilon_F$  happens to be zero, and is referenced to the motive function so that  $\epsilon_i$  represents kinetic energy, then no states available to such a low density of electrons will have a probability of occupancy greater than  $(1/2)$ . For values of  $\epsilon_F$  referred to the motive function that are numerically negative,

as it will be in an isothermal cavity within a conductor, there is no electronic state at that level and yet the Fermi factor of Eq. 3:2 nevertheless expresses the probability that a given quantum state of a definite kinetic energy will be occupied.

This discussion leads to a very practical and at the same time correct means of identifying the Fermi level expressed as  $\epsilon_F$  relative to the motive function and applicable to electron densities for which it is zero or numerically positive. The Fermi energy  $\epsilon_F$  is equal to the energy associated with the quantum level that has a 50 per cent probability of occupancy under the condition of thermodynamic equilibrium.

#### Sect. 4. Flow Equation for Free Electrons and Their Fermi Energy

Even though the electrons within a conductor are acted upon by a very complex, nearly periodic motive function which itself varies with time because of the atomic vibrations, the average value of the electron's total energy as it moves over distances many times the inter-atomic distance, is constant unless a non-conservative interaction alters the energy level occupied by the electron. With this picture in mind, the flow of electrons across boundaries depends on the average momentum associated with an electron moving in a specified direction normal to the boundary of interest. Even though the life-history of an individual electron cannot be followed, thermodynamic equilibrium demands that the rate of loss of electrons from a narrow band of quantum states associated with the range of momentum from  $p_x$  to  $p_x + dp_x$  is equal to the return of electrons to these states. If equilibrium is disturbed by the imposition of a temperature gradient or the application of some external electric field then an electric current can flow or a thermo-electric potential (Thomson EMF) may appear.

The energy distribution function derivable from Fermi statistics and applicable to the free electrons in the cavity described in the previous section is given by

$$f(\epsilon) dx dy dz dp_x dp_y dp_z = \frac{2}{h^3} \frac{dx dy dz dp_x dp_y dp_z}{e^{\frac{\epsilon - \epsilon_F}{kT}} + 1} \quad 4:1$$

In this equation,  $\epsilon$  is the total energy of an electron localized anywhere in the cavity within the range of coordinates  $dx dy dz$  which is sufficiently small so that the potential energy of the electron, that is, its motive can be specified by the coordinates  $x, y$  and  $z$ . The total kinetic energy may be expressed by

$$\text{Kinetic energy} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \quad 4:2$$

If the Fermi level is expressed relative to the motive at the particular space point  $x_1, y_1, z_1$  then the energy  $\epsilon$  may be identified as the kinetic energy of the electron at that point. The number density of electrons in the range of coordinates  $dx, dy, dz$  and their temperature determines the appropriate value for  $\epsilon_F$  which will generally be a negative number within a cavity.

The flow of electrons across a boundary of unit area in unit time demands that they have a component of velocity or momentum perpendicular to the boundary. If the  $x$  direction is the normal to the boundary, and we are interested in those electrons within a narrow range, in the  $x$  component of the momentum, then we must include by integration with respect to  $p_y$  and  $p_z$  all of the electrons that have a particular value of  $p_x$ . If we know this number of electrons and multiply the number by the velocity defined as  $(p_x/m)$ , the resulting equation is

$$v_x d\epsilon_x = \frac{2(2\pi mkT)^{2/2}}{h^3} \ln \left( 1 + e^{-\frac{\epsilon_x - \epsilon_F}{kT}} \right) d\epsilon_x \quad 4:3$$

In this equation the factor  $(2\pi mkT)^{1/2}$  is the direct result of the integration of Eq. 4:1 with respect to either  $p_y$  or  $p_z$  over the entire range of  $-\infty$  to  $+\infty$ . This factor is squared and written as shown in order to call specific attention to the fact that these two integrations have been completed. The kinetic energy associated with the momentum  $p_x$  is defined by

$$\epsilon_x = \frac{p_x^2}{2m} \quad 4:4$$

A restatement of the meaning of Eq. 4:3 is in order. The number of electrons, which cross a boundary in the positive or the negative sense per unit area in one second with kinetic energy between  $\epsilon_x$  and  $\epsilon_x + d\epsilon_x$  when the temperature is  $T$ , is given by this formula. The net current across the boundary within this narrow energy band is zero because the current in positive direction is

precisely balanced by the current in the negative direction.

Although the model used for the derivation of Eq. 4:3 depended on the cavity problem as stated, the result is generally applicable even to the interior region of the metal since it represents a space of constant average motive. Within a distance of the order of  $10^{-8}$  m from the surface, the motive will have changed from its average interior value to that value which in the absence of space charge would have been the motive across the gap of the cavity. Since space charge will always be present in cavities associated with materials and temperatures of interest, the motive will rise to a maximum at the center of the cavity with a gradient depending on the distance from the surface. Its variation is a measure of the space charge present at any specified point. Since in spite of the great change in motive, first sharp and then gradual, the net current across any boundary must be zero in any isothermal cavity and its surround.

The diagram of Fig. 4:1 serves to illustrate the significance of Eq. 4:3 and the fact that in spite of material inhomogeneity, the total absence of current in the isothermal case is associated with the statement that "the Fermi level is continuous." This continuity of Fermi level is only possible by having different values of the Fermi energy  $\epsilon_F$  which is expressed relative to the local motive function. The electron density and therefore the Fermi energy  $\epsilon_F$  at any region in space connected to some other region is dependent on the motive function. In this diagram, the total electron energy associated with the  $x$  direction of motion, is measured in the vertical direction. The positive  $x$  direction is measured from any arbitrary boundary well within the interior of the metal. The average value of the motive at that point will be taken as the reference to which the kinetic energy associated with the motion in the  $x$  direction is added to indicate that the electron is in a quantum level within the band of width  $d\epsilon_{ix}$  at  $\epsilon_{ix}$ . This value of kinetic energy in the metal is identified by the arrow  $\epsilon_{x1}$ . In the immediate neighborhood of the surface, the motive function is shown to change very rapidly an amount designated by  $W_a$ . In a conservative system, the total energy of the electron in passing over this region will remain constant but the proportion of this energy associated with kinetic energy versus potential energy will change as indicated so that the new kinetic energy will be represented by the arrow  $\epsilon_{xa}$ . If the electron proceeds to the center of the cavity, electrical forces due to

space charge will continue this slowing-down process to give the electron its minimum kinetic energy of  $\epsilon_{xc}$ . This minimum in kinetic energy is associated with the maximum in the motive function. This motive change from the interior of the metal to the center of the cavity is shown as  $W_c$ .

In order to satisfy Eq. 4:3 quantitatively at all points along the motive line it is necessary to have the means of relating the local Fermi energy to the local electron density. If the motive function is known and the electron density is known in any single connected region then the correct value of the local Fermi energy can be computed. This computation establishes the position of the Fermi level on the motive diagram. Figure 4:1 is a typical example. There it was assumed that <sup>the</sup> effective density of free electrons in the metal was known. Had the density of free electrons in the center of the cavity been known instead of that in the metal, the location of the Fermi level could have been accurately established relative to the motive function at the cavity center.

Since the Fermi level must be continuous and the Fermi energy is always the energy difference between the Fermi level and the motive function, the electron density in any connected region is determined and varies from place to place depending on the local separation between the motive function and the Fermi level. In order to make such computations quantitative, the basic equation that ties the Fermi energy to the temperature and the number density of electrons will be presented. It will be formulated so as to be applicable for any density and any temperature. This basic equation may be approximated by simplified forms that yield numerical results adequate for nearly all purposes. They are prepared for use to determine the local number density of electrons in terms of the local Fermi energy or to determine the local Fermi energy in terms of the local density.

In any region in which the flow of electrons across a boundary is to be evaluated, it is necessary to know the average electron density and the kinetic energy distribution. The appropriate Fermi energy is found by a direct integration of Eq. 4:1. When energy is expressed relative to the local value of the motive at the coordinate position  $x$ ,  $y$  and  $z$ , and the number of electrons in the region  $dx dy dz$  is  $dn$ , the number density  $\underline{n}$  of the free electrons there is

$$\frac{dn}{dx dy dz} = n = \frac{2}{h^3} 4\pi e^{\frac{\epsilon_F}{kT}} \int_0^{\infty} \frac{p^2 dp}{e^{\frac{p^2}{2mkT} + \frac{\epsilon_F}{kT}}} \quad | \quad 4:5$$



This equation establishes a unique relation between  $n$  and  $\epsilon_F$  at any specified temperature if the random flow of electrons across boundaries is to balance exactly to give no net current in the absence of applied potentials or temperature gradients. Thus if the effective electron concentration  $\underline{n}$  is known, the Fermi energy  $\epsilon_F$  at that location is determined by Eq. 4:5. This equation applies for all temperatures and all realizable densities of free electrons.

The following substitutions are useful

$$S^2 = \frac{p^2}{2mkT} \quad | \quad 4:6$$

and

$$F = \frac{\epsilon_F}{kT} \quad | \quad 4:7$$

Equation 4:5 takes the form

$$n = \frac{2}{h^3} 4\pi (2mkT)^{3/2} e^F \int_0^{\infty} \frac{S^2 dS}{e^{S^2} + e^F} \quad | \quad 4:8$$

Three examples of the use of this equation are of interest:

Case I.  $F$  negative and  $|F| > 4.6$  and therefore  $e^F < 0.01$

$$n_I = \frac{2}{h^3} 4\pi (2mkT)^{3/2} \frac{\sqrt{\pi}}{4} e^F \quad | \quad 4:9$$

$$= 4.83 \times 10^{21} T^{3/2} e^F \quad | \quad 4:9a$$

This equation may be solved for  $F$  to give

$$F = - \ln \frac{2(2\pi mkT)^{3/2}}{h^3 n_I} \quad | \quad 4:10$$

$$= - \ln \frac{4.83 \times 10^{21} T^{3/2}}{n_I} \quad | \quad 4:10a$$

The Fermi energy in joules is then  $\epsilon_F = (kT) F$  and may be expressed in electron volts as  $\epsilon_F = \bar{V} F$ . The electron-volt equivalent of temperature is defined by

$$\bar{V} = \frac{kT}{q} = \frac{T}{11600} = 8.616 \times 10^{-5} T \quad \text{eV} \quad | \quad 4:11$$

Case II  $F = 0$ 

The integral of Eq. 4:8 has a definite value of 0.3390 independent of the temperature. The equation then becomes

$$n_{II} = \frac{2}{h^3} 4\pi (2mkT)^{3/2} 0.3390 \quad |4:12$$

$$= 3.694 \times 10^{21} T^{3/2} \quad |4:12a$$

A comparison between Eq. 4:12 and Eq. 4:9 shows that if the actual density of electrons is less than  $n_{II}$ , Eq. 4:12 may be used and the error in  $F$  will not exceed 0.25 kT and will generally be much less.

Case III  $F$  positive and  $F > 10$ 

Over the range of  $S$  from 0 to  $F^{1/2}$  the following approximation may be used since  $e^{-F}$  is so small.

$$n_{III} = \frac{2}{h^3} \frac{4}{\sqrt{\pi}} (2\pi mkT)^{3/2} \int_0^{F^{1/2}} S^2 dS \quad |4:13$$

The contribution to the density for  $S > F^{1/2}$  is very small. Upon integration we have

$$n_{III} = \frac{2}{h^3} \cdot \frac{4}{\sqrt{\pi}} \cdot \frac{(2\pi mkT)^{3/2} F_0^{3/2}}{3} = \frac{8\pi}{3h^3} (2m)^{3/2} \epsilon_{F_0}^{3/2} \quad |4:14$$

$$= 7.83 \times 10^{74} \epsilon_{F_0}^{3/2} \quad |4:14a$$

Here the energy is in joules and  $n_{III}$  in  $\text{el}/\text{m}^3$ .

This equation may be solved for the Fermi energy to obtain

$$\epsilon_{F_0} = \frac{1}{2m} \left( \frac{h^3}{2} \cdot \frac{3n_{III}}{4\pi} \right)^{2/3} \quad |4:15$$

$$= 5.84 \times 10^{-38} n_{III}^{2/3} \text{ joules} \quad |4:15a$$

$$= 3.646 \times 10^{-19} n_{III}^{2/3} \text{ eV} \quad |4:15b$$

If  $F$  is in the range 1 to 10 a more exact equation is

$$\epsilon_F = \epsilon_{F_0} \left( 1 - \frac{\pi^2}{12} \frac{1}{F_0^2} \right) \quad |4:16$$

Note that  $F_0 = \epsilon_{F_0} / kT$  and that  $\epsilon_{F_0}$  is obtained from Eq. 4:15.

A comparison of Eq. 4:14 and Eq. 4:12 shows that with concentrations greater than that given by Eq. 4:12 as  $n_{II}$ , the Fermi energy computed by Eq. 4:16 will not be in error in the high side more than 0.2 kT and in general the error will be much less.

This analysis shows that the first step in the formulation of quantitative relations is to use Eq. 4:12 to establish the number density of electrons corresponding to the specified temperature. Table 4:1 has been prepared for this purpose. For a number density of electrons less than that recorded in the table, Eq. 4:10 applies and for higher densities Eq. 4:15 supplemented if needed by Eq. 4:16 is used. The table shows that the critical range in electron density is  $10^{25}$  to  $5 \times 10^{26}$  el/m<sup>3</sup>. Equation 4:10 is used for densities below this range and Eqs. 4:15 and 4:16 are used above it.

Table 4:1

Free Electron Density for Zero Fermi Energy as a Function of Temperature

T °K	$T^{1/2}$	$T^{3/2}$	$n_{II}$ el/m <sup>3</sup>	$\bar{V}$ eV
300	17.32	$5.196 \times 10^3$	$1.92 \times 10^{25}$	0.0258
350	18.708	$6.548 \times 10^3$	$2.42 \times 10^{25}$	0.0302
400	20.000	$8.000 \times 10^3$	$2.96 \times 10^{25}$	0.0344
450	21.213	$9.546 \times 10^3$	$3.53 \times 10^{25}$	0.0388
500	22.361	$1.118 \times 10^4$	$4.13 \times 10^{25}$	0.0431
550	23.452	$1.290 \times 10^4$	$4.77 \times 10^{25}$	0.0474
600	24.495	$1.470 \times 10^4$	$5.43 \times 10^{25}$	0.0517
650	25.495	$1.657 \times 10^4$	$6.12 \times 10^{25}$	0.0560
700	26.458	$1.852 \times 10^4$	$6.84 \times 10^{25}$	0.0603
750	27.386	$2.054 \times 10^4$	$7.59 \times 10^{25}$	0.0646
800	28.284	$2.263 \times 10^4$	$8.36 \times 10^{25}$	0.0689
850	29.155	$2.478 \times 10^4$	$9.15 \times 10^{25}$	0.0732
900	30.000	$2.700 \times 10^4$	$9.97 \times 10^{25}$	0.0775
950	30.822	$2.928 \times 10^4$	$1.08 \times 10^{26}$	0.0819
1000	31.623	$3.162 \times 10^4$	$1.17 \times 10^{26}$	0.0862
1050	32.404	$3.402 \times 10^4$	$1.26 \times 10^{26}$	0.0905
1100	33.166	$3.648 \times 10^4$	$1.35 \times 10^{26}$	0.0948
1150	33.912	$3.900 \times 10^4$	$1.44 \times 10^{26}$	0.0991
1200	34.641	$4.157 \times 10^4$	$1.54 \times 10^{26}$	0.1034
1250	35.555	$4.419 \times 10^4$	$1.63 \times 10^{26}$	0.1077
1300	36.056	$4.687 \times 10^4$	$1.73 \times 10^{26}$	0.1120
1350	36.742	$4.960 \times 10^4$	$1.83 \times 10^{26}$	0.1163
1400	37.417	$5.238 \times 10^4$	$1.93 \times 10^{26}$	0.1206
1450	38.079	$5.521 \times 10^4$	$2.04 \times 10^{26}$	0.1249
1500	38.730	$5.810 \times 10^4$	$2.15 \times 10^{26}$	0.1292
1550	39.004	$6.046 \times 10^4$	$2.23 \times 10^{26}$	0.1336
1600	40.000	$6.400 \times 10^4$	$2.36 \times 10^{26}$	0.1379
1650	40.620	$6.702 \times 10^4$	$2.48 \times 10^{26}$	0.1422
1700	41.231	$7.009 \times 10^4$	$2.59 \times 10^{26}$	0.1465

Table 4:1 continued

T °K	$T^{1/2}$	$T^{3/2}$	$n_{II}$ el/m <sup>3</sup>	V eV
1750	41.833	$7.321 \times 10^4$	$2.70 \times 10^{26}$	0.1509
1800	42.426	$7.637 \times 10^4$	$2.82 \times 10^{26}$	0.1551
1850	43.012	$7.957 \times 10^4$	$2.94 \times 10^{26}$	0.1594
1900	43.589	$8.282 \times 10^4$	$3.06 \times 10^{26}$	0.1637
1950	44.159	$8.611 \times 10^4$	$3.18 \times 10^{26}$	0.1680
2000	44.721	$8.944 \times 10^4$	$3.30 \times 10^{26}$	0.1723
2050	45.277	$9.282 \times 10^4$	$3.43 \times 10^{26}$	0.1766
2100	45.826	$9.623 \times 10^4$	$3.55 \times 10^{26}$	0.1809
2150	46.368	$9.969 \times 10^4$	$3.68 \times 10^{26}$	0.1852
2200	46.904	$1.032 \times 10^5$	$3.81 \times 10^{26}$	0.1896
2250	47.434	$1.067 \times 10^5$	$3.94 \times 10^{26}$	0.1939
2300	47.958	$1.103 \times 10^5$	$4.07 \times 10^{26}$	0.1982
2350	48.477	$1.139 \times 10^5$	$4.21 \times 10^{26}$	0.2025
2400	48.990	$1.176 \times 10^5$	$4.34 \times 10^{26}$	0.2068
2450	49.497	$1.213 \times 10^5$	$4.48 \times 10^{26}$	0.2111
2500	50.000	$1.250 \times 10^5$	$4.62 \times 10^{26}$	0.2154
2550	50.498	$1.288 \times 10^5$	$4.76 \times 10^{26}$	0.2197
2600	50.990	$1.326 \times 10^5$	$4.90 \times 10^{26}$	0.2240
2650	51.478	$1.364 \times 10^5$	$5.04 \times 10^{26}$	0.2283

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### Figure Captions

Fig. 4:1 Energy diagram showing motive from the interior of a conductor through a cavity.

Fig. 4:2 Fermi energy dependence on electron density and temperature.

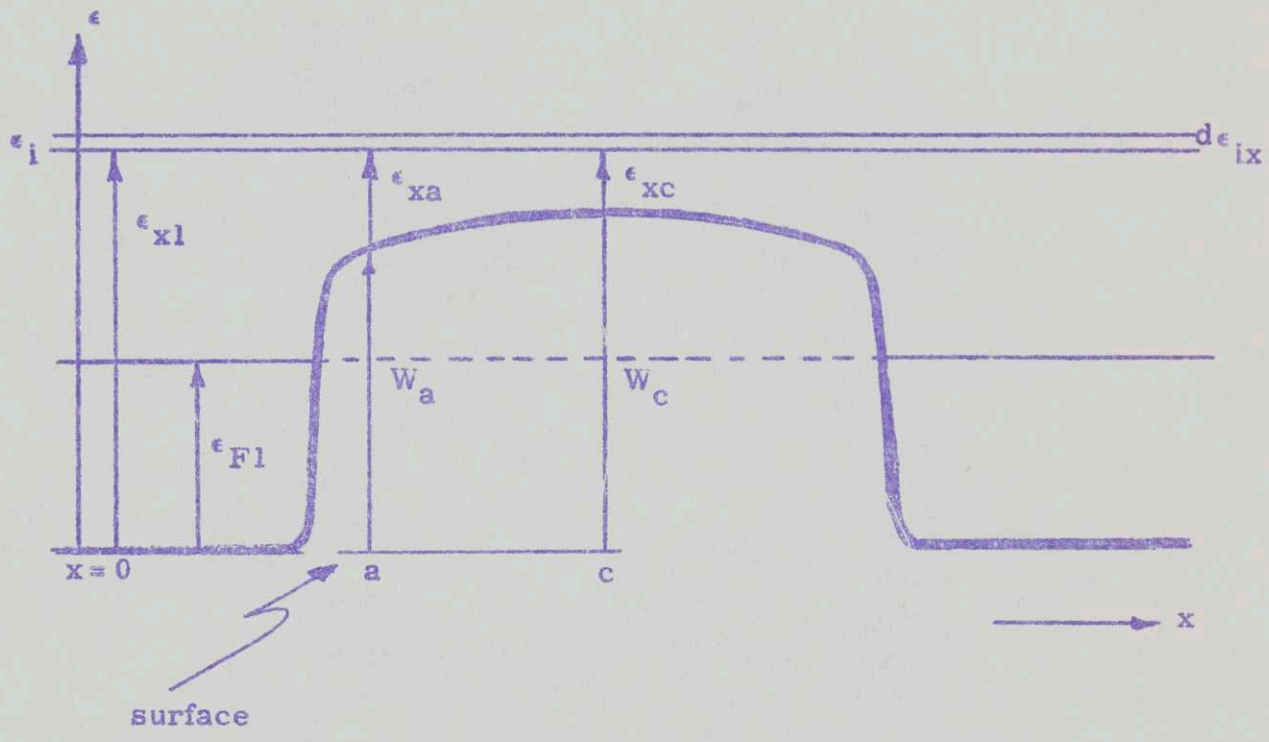


Fig. 4:1



