Abstract—The noble prize winning Richardson-Dushman equation (RDE) had been found to be quite applicable for thermionic emission from metals as far as temperature variation is concerned except the fact that the thermionic emission constant vary from metal to metal contrary to the original equation. We have derived expression for the temperature (T) dependence of work function (W) of a material considering thermal expansion and variation of the chemical potential with temperature. We find that the calculated dW/dT as well as the effective thermionic emission constant, A_0, of metals are fairly in good agreement with experimental results of many metals. We then modify the RDE by using temperature dependent work function and report the excellent fitting of thermionic emission current density data from monolayer graphene with our modified equation. We discuss briefly the potential application of the modified Richardson Dushman equation for thermionic emission from nano-materials. The latter will appear in details in paper II.

Keywords—Work function, temperature dependent chemical potential, modification of Richardson Dushman equation, thermionic emission, thermal expansion coefficient, nano-materials, metals.

I. INTRODUCTION

In a metal the valence electrons of the atoms gets detached from the parent atoms when the atoms form the metal. These valence electrons can move freely within the body of the metal but are held by an electrostatic barrier that prevents them from flying out of the metal under normal circumstances (i.e., at room temperature, no external electric field etc.). As a result of the barrier an electron must have an energy greater than W. This is called the work function W. However, when a metal is heated to high temperature (>700°C) there is a significant number of electrons in the Fermi energy distribution with energy greater than W. Such electrons usually get out of the metal surface in the form of an electron current. This phenomenon, where electrons are emitted from a hot metal surface has been termed as thermionic emission by Owen William Richardson [1,2] who, for his work was awarded Nobel prize. Richardson in his Nobel lecture predicted the form of the dependence of thermionic emission current density J on temperature T. as:

\[ J = A_0 T^2 e^{-W/k_BT} \]  

(1)

Where k_B is the Boltzmann constant. A_0 is a constant with same value for all metals. This equation later became known as Richardson-Dushman (RD) equation. Sommerfield later derived the equation based on free electron theory of metals and showed that A_0 is given by

\[ A_0 = \frac{4\pi e m k_B^2}{\hbar^3} = 1.2 \times 10^6 \text{ A/m}^2\text{K}^2 \]  

(2)

Even though the temperature (T) dependence on J in RD equation (1) was found to hold fairly well, the constant A_0 was found to vary from metal to metal [5,6] and this variation has remained unexplained theoretically so far. Moreover, in Sommerfeld derivation as well as in the original work of Richardson, the work function W was assumed to be independent of temperature, contrary to experiments. Metals have high number density of free electrons (n) and hence the Fermi energy at absolute zero temperature, (E_F0) is also high, usually of the order of a few eV [8a]. This can be understood from the relation

\[ E_{F0} = \left[ \frac{\hbar^2}{2m} \right] \left( \frac{3n}{\pi^2} \right)^{2/3} = 3.65 \times 10^{-19} n^{2/3} \]  

(3)

In nano materials like graphene the surface density of free carriers has been estimated and experimentally determined to be within[8b,c] 10^{12} - 10^{13}/cm². Considering the diameter of carbon atom that makes graphene, this translates to a carrier density [10,11] of 1.6x10^{26} to 1.6x10^{27}/cm³. In the case of metals the free carrier density [8a] 1.15x10^{28} to 1.5x10^{29}/m³. Free carrier density in carbon nano-tube is 7x10^{24}/m³. Free carrier density [14a] in graphite is 7x10^{24}/m³. Maximum
carrier density in carbon nano tube is calculated\textsuperscript{4a} to be 9.9\times10^{23}/m^2. Thus nano materials are expected to have much smaller (E\textsubscript{F0}) than metals. As we shall see in later section the work function is expected to be temperature dependent in such materials. As a consequence the Richardson-Dushman equation should break down in such materials as has been observed[14b]. Metals usually have a small temperature coefficient of work function which, as is shown later, nearly independent of temperature, due to high (E\textsubscript{F0}). Where as in nano-materials \textit{dW/dT} is expected to be temperature dependent as a result of low (E\textsubscript{F0}). This calls for modification of Richardson-Dushman equation, specially, for thermionic emission from nano-materials.

II. RICHARDSON-DUSHMAN EQUATION (RDE) FOR THERMIonic EMISSION FROM A METAL.

It is seen from Table 1 that the effective thermionic emission constant A\textsubscript{0} (=A\textsubscript{a}×b in Table 1) is quite less than the theoretical value of 1.20 \times 10^8 Amp/m\textsuperscript{2}K\textsuperscript{2} for most of the metals except cesium. In the derivation [4] of Eq. 2 it is assumed that the work function, W is independent of temperature, contrary to experimental observation[7,13]. In the next section we consider the temperature dependence of W and modify Eq.1.

III. VARIATION OF WORK FUNCTION (W) OF A METAL WITH TEMPERATURE

The relation of W with T of a pure metal depends primarily on the change of E\textsubscript{F} with T and thermal expansion. To work out this change we rely on the fact that the total number of electrons N(T) in a given piece of metal at T = 0 K is the same as at T = T K. (It is assumed that during thermos electron emission in a thermionic energy converter (TEC), electrons will be replaced at the emitter through load current. The case where electron emission takes place without the electrons being replaced at the emitter will not be treated here). Now at T = 0 K, E\textsubscript{F} = E\textsubscript{F0} and for E< E\textsubscript{F0}, the Fermi function f(E) = 1 at 0 K.

Using the concept of density of state g(E)\textsuperscript{8a} and E\textsubscript{F0}, the total number, N of free electrons in the metal are given by:

\begin{equation}
N(T = 0 (K)) = V \int_0^{E_{F0}} g(E) \, dE \tag{5a}
\end{equation}

at finite temperature T,

\begin{equation}
N(T) = V \int_0^{\infty} g(E)f(E)dE \tag{5b}
\end{equation}

Where

\begin{equation}
f(E) = \frac{1}{1+\exp(E-E_{F0}(T)/k_B(T))} \tag{5c}
\end{equation}

is the well-known Fermi-function. In Eq.5a the upper limit is E\textsubscript{F0}, because at 0 K free electrons fills the energy levels up to E\textsubscript{F0}. In Eq. 5b the upper limit is \infty because at any finite temperature above 0 K, there is a Fermi distribution with energy extending up to \infty.

Considering thermal expansion of the metal,

\begin{equation}
V = V_0 (1 + 3\alpha T) \tag{6}
\end{equation}

Where \alpha = Linear thermal expansion coefficient. Thermionic emission takes place at high temperature (>1000 K). Change of E\textsubscript{F} with T will change the work function W with T [Eq. 4] and this in turn will affect the thermionic emission current density (I) from that given by RDE Equation. This is going to play special role in nano-materials where E\textsubscript{F} is much lower compared to metals [Eq.1], due to much lower concentration of carriers [see results and discussion] at ambient temperature. Our primary objective now is to obtain E\textsubscript{F} and hence W, as a function of T from the equations (4) to (6) and compare with experimental results for metals (Paper I). The 2\textsuperscript{nd} objective is to see how this affects the RD equation and how the modified RD equation fits the experimental results of graphene and carbon nano-tube and detailed comparison with regular (unmodified) RD equation (paper II).

Since N(T=0)= N(T) as discussed above, from eqns. 4 to 6

\begin{equation}
V_0 \int_0^{E_{F0}} g(E) \, dE = V_0 (1 + 3\alpha T) \int_0^{\infty} g(E)f(E)dE \tag{7}
\end{equation}

Now noting that g(E) = 0 for E< 0, the limits 0 to \infty on the RHS of Eq.(7) can be replaced by \infty to \infty. Then following Sommerfeld’s expansion method as explained in Ref.8a, we get from Eq.7,

\begin{equation}
E_F = \frac{E_{F0}^2}{E_F^2} - 3\alpha T E_F - (1 + 3\alpha T)\left[\frac{n^2 (k_B T)^2}{12 E_F} + \frac{7\pi^4 (k_B T)^4}{960 E_F^4}\right] \tag{8}
\end{equation}

The numerical coefficients for successive terms in (8) get smaller and smaller with higher power of T. For temperature T such that K_B T< E\textsubscript{F0}, terms up to the fourth power of T are sufficient.

Eq.(8) is difficult to solve for E\textsubscript{F}. As an approximation by replacing E\textsubscript{F} by E\textsubscript{F0} [assumption valid K_B T< E\textsubscript{F0}] on the RHS of Eq. (8) we get Eq.(9)

\begin{equation}
E_F = -E_{F0} = -3\alpha T E_{F0} - (1 + 3\alpha T)\left[\frac{n^2 (k_B T)^2}{12 E_{F0}} + \frac{7\pi^4 (k_B T)^4}{960 E_{F0}^4}\right] \tag{9}
\end{equation}

Using Eq.(4) we then obtain

\begin{equation}
W(T) = W_0 + 3\alpha T E_{F0} + (1 + 3\alpha T)\left[\frac{n^2 (k_B T)^2}{12 E_{F0}} + \frac{7\pi^4 (k_B T)^4}{960 E_{F0}^4}\right] \tag{10}
\end{equation}

W\textsubscript{0} is the work function of the material at T = 0 K. Eq. (10) gives us the temperature dependence of the work function of a metal. It is interesting to note that W(T) for a given E\textsubscript{F0} increases with T and one shall be able to tune W(T) by tuning the carrier density in nano-materials, as E\textsubscript{F0} depends on carrier density[Eq.1]. It also predicts that in materials with zero E\textsubscript{F0} ,
i.e., in insulator materials, W(T) is infinite, meaning that thermoelectron emission is not possible in insulators. This is in line with experiment. Because of the quantities, α and E_0, this dependence on T is metal specific. The positive temperature coefficients of W(T) from Eq.(10) is consistent with that of many metals [7,13]. We shall examine this in some details in latter section. For temperatures T < E_F_0/k but well below the melting point of the metal, the term with fourth power of T is sufficient. In general the relative contributions of the second, third and fourth terms depend on T and E_F_0.

Eq.(10) is particularly important for estimation of J in materials like graphene, carbon nanotubes etc. with low E_F_0 (0.3 eV). This should also be important for computation of energy distribution[15] of emitted electrons from nanomaterials. For metals where E_F_0 > a few eVs, the work function, dW(T)/dT in [Eq. 10] is practically temperature independent for T ~ 2000 K which means metals have almost a linear variation of W with T. In such cases the second term in Eq.10 dominates the third and the fourth terms. For greater accuracy in computation of W the eq. 7 needs to be solved numerically, which is quite tedious and not easily applicable for computation of thermionic emission current density.

IV. NEW MODIFIED RICHARDSON DUSHMAN EQUATION (MRDE)

Richardson Dushman equation for thermoelectron current density (emitted along z direction) is given by:

\[
J = \int dnev_x = \int \int f_{v_x} f_{v_y} f_{v_z} w_{v_x} = 0, v_y = 0 [2e^2 m^3 \exp \left( \frac{E_F}{k_BT} \right)] \times \exp \left( - \frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_BT} \right) dv_x dv_y dv_z
\]

where v_x_0 is the minimum velocity required for electron to get out of the metal in the z direction (direction of electron emission) and is given by:

\[
v_x_0 = \sqrt{2 \left( E_F + W(T) \right)} / m
\]

From Eqs. (10) - (12) we finally get the modified Richardson-Dushman thermoelectronic emission equation (MRDE) for J as

\[
J = A_0 T^2 \exp \left( - \frac{W_0 + 3\alpha TE_F_0 + (1 + 3\alpha T) \left( \frac{m^2 (k_B T)^2}{E_F_0} \right) \frac{7\pi^4 \left( k_B T \right)^4}{960 E_F_0^2} \right) \right] / k_B T)
\]

Eq. 13 gives us new modified thermoelectron emission equation that must be applied for materials like graphene, carbon nanotubes which have low E_F_0 and at temperatures comparable to E_F_0/k_B. For E_F_0 of the order of 0.3 eV and for T within 2500 K, terms up to fourth order in Eq.13 is sufficient, since the contribution of the sixth power of T will be negligible. For metals with high E_F_0 (a few eVs), at temperatures k_B T < E_F_0, Eq. 13 approximately gives the ordinary RD temperature dependence with an effective thermoelectron emission constant A_eff (Eq.14).

Eq. 13 gives us the modified thermoelectron emission equation with the constant A_0 changed to a new constant A_eff

\[
A_{eff} = A_0 \exp \left( - \frac{3E_F_0}{k_B} \right)
\]

Now in Eq. (14) the term E_F_0/k_B is a constant of a given metal and is metal specific. E_F_0 is given by Eq.3. The number density n can be calculated from, n = zNA ρ/M, z = valency; ρ = density; M = atomic mass. NA = Avogadro number. n can also be calculated from the following relation: n = xz/a_3. Where x = number of atoms per unit cell of the metal crystal. z = valency of the metal, a = lattice constant of the metal. n of some metals calculated from the second relation is given in Table 1. E_F_0 is then computed from Eq.(3). The nearly temperature independence of the thermal expansion coefficient α can be understood from the following considerations:

\[
\alpha = \frac{\gamma (c \rho_{\text{ion}} + c \rho_{\text{el}})}{3\beta}
\]

Where γ is the overall Gruneisen parameter of the metal; this is primarily of the order of unity and temperature independent. β the bulk modulus. At temperatures above 300 K, C_v^{\text{penn}} assumes the value of 3R. C_v^{\text{el}} is usually much smaller than C_v^{\text{ion}}. The electronic contribution C_v^{\text{el}} is very negligible at high temperature. Thus α can be assumed to be fairly independent of temperature in a metal. For greater accuracy temperature dependence of α can be inserted in Eqs.7, 10 & 13.

This new thermionic constant[A_0] A_eff is dependent on two quantities: α and E_F_0 which are both metal specific. It is to be noted that the Schottky effect (lowering of work function by the presence of electric field, E on to the metal surface) modification of the thermoelectric emission equation that is well-known is not added to eq.13. With Schottky- effect Wo is lowered to W_0’ (Eq.16).

\[
W_0’ = W_0 - e \left( \frac{E_F}{4\pi e_0} \right)^{0.5}
\]

The final modified equation for thermoelectric emission is given by:

\[
J = A_0 T^2 \exp \left( - \left( W_0 + 3\alpha TE_F_0 + (1 + 3\alpha T) \left( \frac{m^2 (k_B T)^2}{E_F_0} \right) \frac{7\pi^4 \left( k_B T \right)^4}{960 E_F_0^2} \right) \right] / k_B T)
\]

Eq. (17) can be said to be the final modified RD equation that takes care of Schottky effect, thermal expansion and change of chemical potential with temperature.

Because Fermi surface of a metal is not spherical in k-space, E_F_0 can depend on crystallographic orientation of the metal plates from which thermoelectric emission takes place and hence A_eff. In Eq. 10, for metals with E_F_0 of a few eVs, at temperatures up to 2500 K, dW/dT is primarily due to thermal expansion of metals. Since deviation of A_eff [Eq.14] from A_0 is primarily due to thermal expansion of materials, A_eff and dW(T)/dT of a given metal can also depend on whether thermoelectric emission measurement is carried out on (i) thin wire; (ii) plate surface; (iii) spherical surface or cubical surfaces of the metal. At thermoelectric emission temperature of 900 K the de Broglie wavelength of electron is 41 Angstrom and it decreases with higher temperature. As long as the two dimensional plate thickness or the diameter of a long wire is significantly greater than 41 angstrom, three dimensional density of states and hence Eqs. (8 -14) will be valid for thermoelectric emission from plate surface and the cylindrical.
surface of a wire. However, the effect of thermal expansion for three dimensional, two dimensional (thin plate) and one dimensional (thin wire) emitters can be accounted for by replacing $3\alpha$ in Eqs. 10, 13 and 17 by $r\alpha$ where $r=1,2$ and 3 for thermos electronic emitters in the shape of thin wire, a thin plate and a bulk cube or sphere.

III. 3. Rate of change of work function and effective thermionic constants of metals:

With this idea $A_{eff}$ and $dW/dT$ for electron emissions from metal at temperatures $k_B T << E_{F0}$ can be given by:

$$A_{eff} = A_0 \exp \left(-r\alpha \frac{r\alpha E_{F0}}{k_B}\right)$$  \hspace{1cm} (18) $$

$$
\frac{dW(T)}{dT} = r\alpha E_{F0}
$$  \hspace{1cm} (19) $$

where $r=1,2$ and 3 for thermos electronic emitters in the shape of thin wire, a thin plate and a bulk cube or sphere respectively. Eq.(19) is valid for most metals as $E_{F0} > 2$ eVs.

$$a = \left(\frac{dW}{dT}\right)_{exp} \times 10^{-4} \text{ eV/K, } b = \left(\frac{dW}{dT}\right)_{th} \times 10^{-4} \text{ eV/K}$$

<table>
<thead>
<tr>
<th>Metal</th>
<th>W (eV)</th>
<th>A×b (Acm^-2K^-2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molybdenum</td>
<td>4.15</td>
<td>55</td>
</tr>
<tr>
<td>Nickel</td>
<td>4.61</td>
<td>30</td>
</tr>
<tr>
<td>Tantalum</td>
<td>4.12</td>
<td>60</td>
</tr>
<tr>
<td>Tungsten</td>
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<tr>
<td>Barium</td>
<td>2.11</td>
<td>60</td>
</tr>
<tr>
<td>Cesium</td>
<td>1.81</td>
<td>160</td>
</tr>
<tr>
<td>Indium</td>
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<td>170</td>
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<td>Platinum</td>
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<tr>
<td>Rhenium</td>
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<td>100</td>
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<tr>
<td>Thorium</td>
<td>3.38</td>
<td>70</td>
</tr>
<tr>
<td>Ba on W</td>
<td>1.56</td>
<td>1.5</td>
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<td>Cs on W</td>
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</tr>
<tr>
<td>Th on W</td>
<td>2.63</td>
<td>3.0</td>
</tr>
<tr>
<td>Thoria</td>
<td>2.54</td>
<td>3.0</td>
</tr>
<tr>
<td>BaO + SrO</td>
<td>0.95</td>
<td>$-10^2$</td>
</tr>
<tr>
<td>Cs-oxide</td>
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<td>TaC</td>
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<td>LAB₆</td>
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<td>Theoretical</td>
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<td>120.2 (b=1)</td>
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<table>
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<tr>
<th>Metal</th>
<th>W</th>
<th>a</th>
<th>b</th>
<th>Tm (K)</th>
<th>$E_{F0}$ (eV)</th>
<th>$\sigma \times 10^{-6}$ /K</th>
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<tr>
<td>Ga</td>
<td>4.07</td>
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<td>7.3&quot;</td>
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<tr>
<td>In</td>
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<td>4.36&quot;</td>
<td>429</td>
<td>8.63</td>
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<tr>
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<td>2.41&quot;</td>
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<tr>
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<td>1.29&quot;</td>
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<tr>
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<td>606.6</td>
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TABLE III. COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES* OF THERMIONIC EMISSION CONSTANT $A^\prime$

\[ C = A_{eff}/(k_B\times 10^4(Acm^{-2}K^{-2}) \text{ AND } d = A_{eff(exp)} \times 10^4(Acm^{-2}K^{-2}) \]

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\alpha \times 10^{-4}/C$</th>
<th>$n(10^{20}/m^3)$</th>
<th>$E_{F_0}(eV)$</th>
<th>$C$ [r=1]</th>
<th>$C$ [r=2]</th>
<th>$d$</th>
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<tr>
<td>Ca</td>
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<td>35.3</td>
<td>60 [30]</td>
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<tr>
<td>Cr</td>
<td>6.2 [28]</td>
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<td>7.05</td>
<td>72.3</td>
<td>48 [30]</td>
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<tr>
<td>Cs</td>
<td>97 [28]</td>
<td>0.90</td>
<td>1.59</td>
<td>20</td>
<td>162 [30]</td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>6.5 [28]</td>
<td>11.03</td>
<td>8.38</td>
<td>63.8</td>
<td>60 [30]</td>
<td></td>
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CONCLUSION

Original Richardson-Dushman thermionic emission equation is based on temperature independent work function $W$ which gives thermionic emission equation with emission constant $A$ same for all metals. Experiments confirm that $A$ varies from metal to metal and $W$ varies with temperature. We have considered temperature variation of work function of metals taking into account thermal expansion and temperature variation of chemical potential to obtain theoretical expression for temperature dependent work function (Eq.10) and modified Richardson-Dushman equation (Eq. 13 or 17). We have seen fairly good agreements for several metals on $dW/dT$ and $A_{eff}$ with not so good agreement for alkali metals. To our knowledge there is no unified single theory that explains the experimental observations of $A_{eff}$ and $dW/dT$ for all metals and the thermionic emission from nano-materials. This modified equation does not affect the temperature dependence of thermionic emission current density much from the original RD law for metals because metals have high $E_{F_0}$ compared to $k_BT$. It will however, significantly alter the temperature dependence for nano-materials which have low $E_{F_0}$. It is reported that the ordinary RD law cannot explain the experimental thermionic emission current data for graphene [22] and carbon nanotubes [14b]. We have verified that our model fits the data excellently well. We have seen that the values of thermal expansion coefficient and the carrier density derived from the fitting agree very well with independent experimental measurements. The excellent agreement of thermionic emission current density of monolayer graphene with our theory provides further validity of our theory-this aspect will be detailed in subsequent publications along with the detailed applications of the modified RD equation to nano-materials. The equation is expected to be important also in the studies of the energy distribution of thermally electrons from nano-materials [15] and for correct evaluation of performance of the energy converter for solar thermionic power conversion using nano-materials.

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