ON THE KINETIC THEORY OF THE THERMIONIC EFFECT

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Abstract

Making different assumptions as to the behavior of electrons inside a solid body, statistical deductions for the thermionic currents in the corresponding cases are made. All the formulas obtained are of the type $i = AT^a e^{-b/T}$ and differ only in the values of A and a. The following cases are investigated. (1) The electrons inside a body are assumed to behave like a perfect gas. In this case a comes out $1/2$. (2) The electrons are assumed to be arranged in a space-lattice with the same dynamical properties as the ordinary crystal-lattices. For this case $a = -1$. (3a) All electrons are assumed to be moving on quantized orbits with the same quantum number and energy. For this case $a = 2$. The case (3b) in which the electrons inside the metal are assumed to be divided into S groups, each group i moving in an orbit with the quantum number i, is more complicated and will be discussed in a separate paper. The experimental results are at present not accurate enough to decide between these values of a.

I. The problem of emission of electrons from hot bodies is usually regarded as a problem of evaporation. Therefore thermodynamic considerations applied to the thermionic effect lead to expressions similar to those applied to evaporation.

The thermodynamic expression for the vapor-pressure[1] is

$$p = \text{const. } T^{-(c-c_p)/R} e^{-\lambda/T} \tag{1}$$

λ being a constant (the heat of evaporation), c the heat capacity of the solid, c_p the heat capacity of the vapor at constant pressure, and R the gas constant.

At this point the pure thermodynamic method is exhausted. Without making further hypotheses as to the connection between c, c_p and R, hypotheses which are more of a kinetic character than thermodynamic, we are unable to determine the power of T in (1). For monatomic gases we have $c_p = (5/2)R$, and assuming the validity for the solid of the law of Dulong and Petit we have $c = 3R$. Then (1) reduces to

$$p = \text{const. } \times T^{-\frac{1}{2}} e^{-\lambda/T} .$$

The effect of different kinetic assumptions on the final result is explicitly seen in different *kinetic* deductions of the vapor-pressure formulas; due to this difference of assumptions involved, P. Ehrenfest and V. Trkal,[2]

[1] W. Nernst, Theoretical Chemistry, 10th German ed., trans. by N. Godd, p. 68 (1923).

[2] Ehrenfest and Trkal, Amst. Proc. **23**, p. 182 (1920).

D. Enskog[3] and R. H. Fowler[4] arrived at different values of the power of T, although all their formulas are of the same type as (1).

The formulas for the number of electrons emitted by a hot body also vary according to the assumptions involved.

The purpose of the present investigation is to deduce on a purely kinetic basis formulas for the thermionic current, under different special assumptions as to the behavior of electrons inside the metal. All the formulas will be of the type

$$i = A T^a e^{-b/T} \tag{2}$$

the exponent a depending on the assumptions involved.

Even without any kinetic investigation, by pure thermodynamic reasoning we may find the physical meaning of the hypothesis which leads to $a=2$. Formula (1) may be applied to the electrons outside the metal. Remembering now that p is connected with n_0 by the expression

$$p = n_0 kT \tag{3}$$

and n_0 is connected with i by

$$i = n_0 \epsilon \sqrt{kT/2\pi m} ,$$

we see that to a power d of T in (1) corresponds a power of T equal to $d-\frac{1}{2}$ in (2). To obtain therefore $a=2$ in (2) we must have

$$(c-c_p)/R = 5/2 . \tag{4}$$

Now there can be little doubt that if it is admissible to consider the outside electrons as a perfect gas, we must consider it as a monatomic one, so that we have in any case

$$c_p = (5/2)R . \tag{5}$$

It follows immediately, then, that (4) may be obtained only by putting $c=0$, that is by assuming the energy of the internal electrons to be zero, or at least independent of the temperature. This assumption in slightly different forms is made by both S. Dushman and S. Roy.[5]

In any other case we will obtain values for a different from 2; and as it is evident that the assumption $c=0$ is only a more or less close approximation, we see at once that $a=2$ is also only an approximation.

II. We now proceed to the investigation of different possible typical assumptions as to the electrons inside the metal.

These may be of the three following kinds:

(1) The electrons inside the metal are free and behave like an ideal gas. Their energy is only kinetic.

[3] Enskog, Ann. der Phys. **72**, 321 (1923).

[4] Fowler, Phil. Mag. p. 30 (1923); on p. 31 is given a comparison of different formulas.

[5] Dushman, Phys. Rev. **21**, 623 (1923); Roy, Phil. Mag. **47**, 561 (1924).

(2) The electrons are bound, and form a space-lattice, like the positive ions, and are held in their equilibrium positions by quasi-elastic forces, the displacements being small.

(3) The electrons are bound, but do not form a space lattice. They move on quantized orbits. The orbit of an electron may belong either to a single positive ion, or to the crystal[6] as a whole. As J. Frenkel points out, this second possibility is the *most probable from the point of view of electrodynamics.*

In all three cases it is assumed that outside the hot body the electrons behave like a perfect gas. As to the statistical methods of treating our problem, we will use that employed by M. Born in his deduction of the formula for vapor-pressure.[7]

III. *Case (1). Electrons assumed to be free.* Suppose from N electrons, available for distribution, n are outside and n' inside the metal. Denote the work necessary to remove all n electrons from the metal by $G=ng$, g being the average work per electron. Denote further by p_i $(i=1, 2 \ldots 3n)$ the momenta of the outside electrons; then the total energy of these electrons is

$$E_e=(1/2m)\sum_{i=1}^{i=3n} p_i^2+ng \tag{6}$$

m being the mass of an electrons.

In the same way, for the inside electrons we find

$$E_i=(1/2m)\sum_{i=1}^{i=3n'} p_i'^2 \tag{7}$$

p_i' being the momenta.

The probability that the electrons 1, 2, 3, ... $3n$ are outside while $(n+1)$, $(n+2)$, ... N are inside the metal is

$$W'=A\int e^{-(1/kT)\,(Ee+Ei)}\,dq_1 \ldots dp_{3n}dq'_1 \ldots dp'_{3n'}\,, \tag{8}$$

q_i and q_i' being the coordinates of the outside, and inside electrons respectively. The integration over these variables is to be taken over all the outside volume V and all the inside volume V' of the metal, respectively. The integration over p_i and p_i' is to be taken from $-\infty$ to $+\infty$. This gives

$$W'=Ae^{-ng/kT}V^nV'^{n'}(2\pi mkT)^{3N/2}\,. \tag{9}$$

[6] J. Frenkel, Zeits. f. Phys. **29**, 214 (1924).

[7] M. Born, Atomtheorie des festen Zustandes, Encykl. der Math. Wiss., Band V_3, Heft 4, p. 705.

To obtain the probability that any n electrons are outside and any n' inside the metal, we have to multiply W' by $N!/n!n'!$ This gives

$$W = A(N!/n!n'!)e^{-ng/kT}V^nV'^{n'}(2\pi mkT)^{3N/2} . \tag{10}$$

The equilibrium state is defined by the maximum of log W. Using Stirling's formula, $\log n! = n \log n - n$, and putting $d \log W/dn = 0$, we find

$$\log n = -g/kT + \log (N-n) + \log V/V' \tag{11}$$

or

$$n(N-n) = (V/V')e^{-g/kT} . \tag{12}$$

We introduce now the concentration $n_0 = n/V$ of the outside electrons and $n_0' = n'/V'$ of the inside ones. n_0' may be considered as constant because $n' = N-n$ is approximately equal to N; N being about 10^{10} larger than n.[8] We obtain

$$n_0 = n_0' e^{-g/kT} , \tag{13}$$

and for the thermionic current we obtain finally the expression

$$i = \sqrt{k\epsilon^2 n_0'^2/2\pi m}\, T^{\frac{1}{2}} e^{-g/kT} \tag{14}$$

IV. *Case 2. Electrons assumed bound in a space-lattice.* The n electrons arranged in a space-lattice perform vibrations with $3n'$ frequencies ν_i $(i = 1, 2, \ldots 3n')$. Their potential energy is in general a function of the coordinates of all electrons and ions in the space-lattice, but by the introduction of normal coordinates[9] it can be brought to the form

$$\tfrac{1}{2}\sum_{i=1}^{i=3n'} \omega_i^2 q_i'^2 , \tag{15}$$

while if p_i' are the momenta corresponding to the normal coordinates q_i', the kinetic energy is equal to

$$\tfrac{1}{2}\sum_{i=1}^{i=3n'} p_i'^2 . \tag{16}$$

We have therefore,

$$E_i = \tfrac{1}{2}\sum_{i=1}^{i=3n'} (p_i'^2 + \omega_i^2 q_i'^2) , \tag{17}$$

while the expression (6) remains for the outside electrons.

We follow now the method used by Born in the deduction of the vapor-pressure formula, and find

$$\log n = -g/kT + \log V - (3/2)\log T + (3/2)\log (2\pi\nu_0^2 m/k)$$

or

$$n_0 = (2\pi\nu_0^2 m/k)^{3/2} T^{-3/2} e^{-g/kT} \tag{18}$$

[8] Richardson, Emission of Electricity from Hot Bodies, 2nd ed. (1921) p. 40.

[9] M. Born. loc. cit.[7] p. 593.

where

$$\nu_0^{3n'} = \prod_{i=1}^{i=3n'} \nu_i \ . \tag{19}$$

Hence

$$i = (2\pi m \nu_0^3 \epsilon / k) T^{-1} e^{-g/kT} \tag{20}$$

V. *Case 3. Electrons assumed bound in orbits.* This may be subdivided in two sub-cases:

(a) All electrons inside the metal move on orbits with the same quantum number, i. e. with the same energy e.

(b) The n' electrons inside the metal are divided into s groups, each electron of a group i ($i = 1, 2, \ldots s$) moving in an orbit with the quantum number i and having thus the energy e_i; the number of electrons in the i-group is n_i'. Thus $n' = \sum_1^s n_i'$.

For the subcase (a) we have

$$W' = A e^{-n'e/kT} \int e^{-Ee/kT} dp_1 \ldots dq_1 \ldots \tag{21}$$

E_e being given by (6).

Thus

$$W' = A e^{-(N-n)e/kT} e^{-ng/kT} V^n (2\pi m k T)^{3n/2} \tag{22}$$

To obtain W we multiply only by $N!/n!n'!$, but do not need to multiply by $n'!$ as all orbits are similar. In the case of a space-lattice formed by n electrons, two electrons chosen at random differ in general by their frequences as there are $3n$ frequencies for n electrons. There is thus *a physical* difference between them, while in the case of absolutely similar orbits no such difference exists. Thus we finally obtain by computing W and putting $d \log W/dn = 0$,

$$\log n - \log (N-n) = \log V - (g-e)/kT + 3/2 \log (2\pi m k T)$$

or introducing again n_0, and putting n' for $N-n$

$$n_0 = n' (2\pi m k)^{3/2} T^{3/2} e^{-(g-e)/kT} \tag{23}$$

or

$$i = 2\pi n' \epsilon m k^2 T^2 e^{-(g-e)/kT} \ . \tag{24}$$

The factor T^2 in this case is due to the fact that we have assumed the energy E_i of the electrons in the crystal to be $n'e$, i. e. independent of T, and therefore we have in (1) $c = dE/dT = 0$.

In the subcase (b) things are much more complicated. We have

$$W' = A \prod_{i=1}^{i=s} e^{-n_i' e_i'/kT} \int e^{-E_e/kT} \, dq_i \ldots dp_i \ldots \tag{25}$$

and to obtain W we must multiply W' by

$$N!/n!n_1!n'_2 \cdot \ . \ . \ . \ n_s'!$$

W is a function of n and of any $(s-1)$ of the n_i' the remaining one n_i' being given by the equation

$$n+\sum_{i=1}^{i=s} n_1' = N \ .$$

We have the equations

$$dW/dn=0 \ ; \ dW/dn_1'=0 \ ; \ . \ . \ . \ dW/dn_i'=0$$

from which we find n and n_i'.

The explicit solution of the problem requires the knowledge of the function giving the energies e_i in terms of quantum numbers. We may also simplify the problem by assuming that the partition function of the inside electrons is not considerably altered by the emission, and therefore n_i' are known functions of e_i and T.

The case 3b seems to be the most plausible and will be investigated in another paper. We did not apply the quantum theory when dealing with space-lattices. This, of course, limits the application of our considerations to high temperatures, when the quantum theory degenerates into the classical one and the law of equipartition holds with greater approximation. Experimentally we nearly always use this range of temperatures.

It is noteworthy that the experimental results do not allow us up to the present time to make a choice between the different cases discussed in this paper. In a quite recent article[10] Dushman, Rowe, Jessie Ewald and Kidner give the results of very accurate measurements on tungsten, molybdenum and tantalum. They find that the points representing $\log i - 2 \log T$ as a function of $1/T$ fall very accurately on a straight line. Unfortunately, a very close agreement is obtained also in plotting $\log i - \frac{1}{2} \log T$ (which corresponds to $a=\frac{1}{2}$) or $\log i + \log T$ (which corresponds to $a=-1$). Using the values given in the Table V of the article mentioned, plots were made and it was found that no preference can be given to any of the expressions.

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[10] Dushman, Rowe, Ewald and Kidner, Phys. Rev. **25**, p. 338 (1925).