A REVIEW OF THE THEORY OF METALLIC CONDUCTION

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I. PROBLEM OF ELECTRICAL AND THERMAL CONDUCTION

The transport of electricity or of heat by metals is assumed to be effected principally through the agency of free electrons. These, under normal conditions of the metal, are assumed to be in statistical equilibrium, for which a distribution function f_0 exists, such that

$$f_0\ (\xi,\ \eta,\ \zeta)\ d\xi\ d\eta\ d\zeta$$

gives the number of electrons per unit volume the velocity components of which lie between ξ and $\xi + d\xi$, η and $\eta + d\eta$, ζ and $\zeta + d\zeta$. It follows that n, the total number of electrons per unit volume, is given by the expression:

$$\int f_0\ (\xi,\ \eta,\ \zeta)\ d\lambda;$$

in this expression $d\lambda$ is an element of the velocity-space equal to $d\xi d\eta d\zeta$, and the integration is to be extended over all values of the velocities. It follows also that, under normal conditions, the excess number of electrons passing (in the positive direction over the number passing in the negative direction) per second through a unit plane perpendicular to the direction corresponding with the ξ-component is

$$\int \xi f_0\ (\xi,\ \eta,\ \zeta)\ d\lambda = 0 \tag{1}$$

Under the influence of a difference of potential or of a temperature gradient in the metal, the distribution function is altered,

$f(\xi, \eta, \zeta)$ replacing $f_0(\xi, \eta, \zeta)$, giving rise to a stream of electrons corresponding with the direction of the impressed force or of the temperature gradient. In the case of a difference of electrical potential applied in the direction of ξ, the current per unit cross-section is

$$J = e \int \xi f\,(\xi, \eta, \zeta)\, d\lambda, \tag{2}$$

where e is the charge on the electron; correspondingly, in the case of a temperature gradient, the quantity of kinetic energy transferred per second per unit cross-section is

$$W = \frac{m}{2} \int v^2\, \xi f\,(\xi, \eta, \zeta)\, d\lambda \tag{2a}$$

where m is the mass of the electron and $v^2 = \xi^2 + \eta^2 + \zeta^2$.

In the absence of collisions, the electrons which at a given time are in the element of volume dS of the metal and the representative points of which in the velocity-space lie in $d\lambda$, after the lapse of time dt, are in an element of volume dS' of the metal, equal to dS, and their representative points in the velocity-space lie in $d\lambda'$, equal to $d\lambda$. The electrons of the group considered have initially the same components of velocity, or with only infinitesimal variations, since their representative points lie in $d\lambda$. Under the influence of a force giving rise to an acceleration X in the direction of the x-axis (i.e., the direction of ξ), operating during a time dt, ξ is altered to $\xi + Xdt$, x to $x + \xi dt$, y to $y + \eta dt$, z to $z + \zeta dt$; η and ζ remain unchanged. Since, in the absence of collisions, the number of electrons (reckoned per unit volume) characterized initially by $\xi, \eta, \zeta, x, y, z, t$ is equal to the number characterized, after the lapse of time dt, by the altered quantities just given, it follows necessarily that:

$$f\,(\xi, \eta, \zeta, x, y, z, t) = f\,(\xi + Xdt, \eta, \zeta, y + \eta\, dt, x + \xi\, dt, z + \zeta\, dt, t + dt) \tag{3}$$

During the passage of a group of electrons from $(dS, d\lambda)$ to $(dS', d\lambda')$, however, the number in the two groups does not in general remain the same on account of collisions. If b is the number of electrons joining the group per second as a result of collisions and a the number leaving it, then

$$f(\xi, \eta, \zeta, x, y, z, t) + (b - a)\,dt = f(\xi + X dt, \eta, \zeta, x + \xi\,dt, y + \eta\,dt, z + \zeta\,dt, t + dt) \qquad (3a)$$

Since the right-hand side of equation (3a) may be replaced by:

$$f(\xi, \eta, \zeta, x, y, z, t) + \frac{\partial f}{\partial \xi} X dt + \frac{\partial f}{\partial x}\xi\,dt + \frac{\partial f}{\partial y}\eta\,dt + \frac{\partial f}{\partial z}\zeta\,dt + \frac{\partial f}{\partial t}dt$$

and since the function f is assumed constant in y, z, t for a steady-state condition arising from a force in the x-direction, it follows that:

$$b - a = \frac{\partial f}{\partial \xi} X + \frac{\partial f}{\partial x}\xi \qquad (4)$$

In order to simplify the calculation of $(b - a)$, the atoms are considered as rigid, elastic spheres; further, the atoms are considered as immovable on account of their relatively large masses, and the mutual collisions between electrons are ignored. The number of collisions between electrons of the group $(d\lambda)$ and metal atoms, such that the line of centers lies within a solid angle dw (equal to $\sin\vartheta\, d\vartheta\, d\varphi$) is first to be considered. ϑ is the angle between the line of centers (at the moment of impact) and the direction of the velocity of the electron (figure 1); φ is the dihedral angle between the plane POx (formed by the x-axis and a line drawn from the origin in the direction of the velocity) and the plane POQ (formed by two lines drawn from the origin of coördinates, one in the direction of the line of centers at impact, the other in the direction of the velocity). The velocity component in the direction of the line of centers at impact is $v \cos \vartheta$. Electrons colliding in the manner specified must lie at the moment of impact on a surface-element of a sphere, the radius R of which is equal to the sum of the effective radii of atom and electron. This surface-element is $R^2 \sin\vartheta\, d\vartheta\, d\varphi$. All electrons of the group having positions at a given moment within a distance equal to $v \cos \vartheta$ collide in the manner specified during the ensuing unit of time. The volume therefore containing electrons colliding during a second in the specified manner is $R^2 v \cos\vartheta \sin\vartheta\, d\vartheta\, d\varphi$ and since there are $f(\xi, \eta, \zeta)d\lambda$ electrons per unit volume in the group, the number of such collisions per second by electrons of the group with one metal atom is

$$f\ (\xi\ \eta\ \zeta)\ d\lambda \cdot R^2\ v\ \cos\vartheta\ \sin\vartheta\ d\vartheta\ d\varphi$$

If there are n metal atoms per unit volume, the total number of collisions per unit volume per second by electrons specified by ξ, η, ζ such that the angle between the line of centers at impact and the direction of the velocity lies within the solid angle dw is

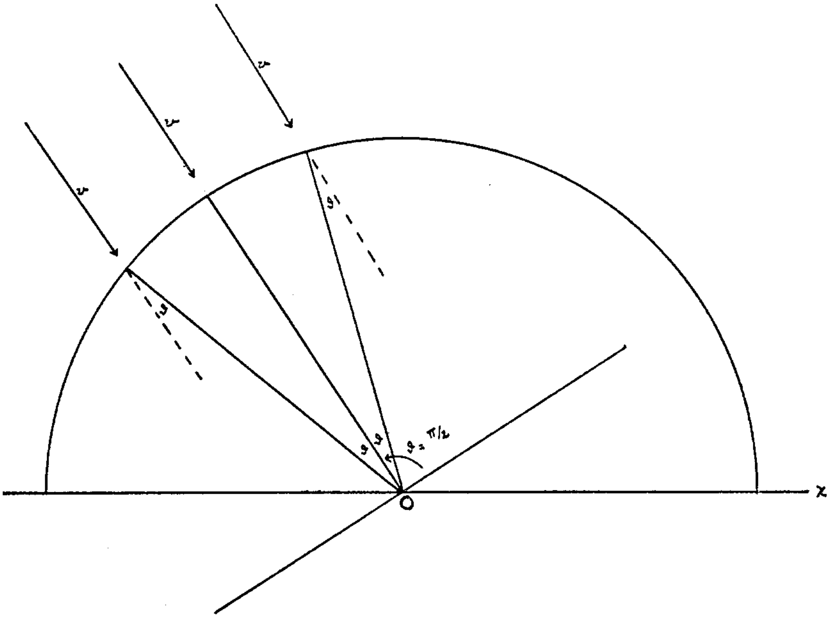

FIG. 1. GEOMETRICAL RELATIONSHIPS AT IMPACT

$$n\ R^2\ v\ f\ (\xi, \eta, \zeta)\ d\lambda \cdot \cos\vartheta\ \sin\vartheta\ d\vartheta\ d\varphi \tag{5}$$

The velocity-point of the deflected electron may be found by a consideration of the fact that the velocity-component parallel to the direction of the line of centers at impact is reversed, while that perpendicular to it persists. Reference to the simplified, two-dimensional diagram of figure 2 (see p. 144) shows the nature of the results:

$$\angle 1 + \angle 2 + \angle 3 = \frac{\pi}{2}$$

$$\angle 1 + \angle 2 = g$$

$$\angle 2 + \angle 3 = \vartheta' = \vartheta$$

whence

$$\angle 2 = g + \vartheta - \frac{\pi}{2}$$

$$\sin \angle 2 = \frac{\xi'}{v'} = \frac{\xi'}{v} = - \cos (g + \vartheta) = \sin g \sin \vartheta - \cos g \cos \vartheta \tag{5a}$$

$$\alpha = \pi/2 - \vartheta$$

$$\alpha + g = \pi/2 + (g - \vartheta)$$

$$\sin (\alpha + g) = \frac{\xi}{v} = \cos (g - \vartheta) = \cos g \cos \vartheta + \sin g \sin \vartheta \tag{5b}$$

From a comparison of equations (5b) and (5a), it follows that:

$$\frac{\xi'}{v} + \cos g \cos \vartheta = \frac{\xi}{v} - \cos g \cos \vartheta \tag{6}$$

or,

$$\xi' = \xi - 2\, v \cos g \cos \vartheta \tag{6a}$$

By analogy,

$$\eta' = \eta - 2\, v \cosh \cos \vartheta \tag{7}$$

$$\zeta' = \zeta - 2\, v \cos i \cos \vartheta \tag{8}$$

The angles g, h, i are those between the direction of the line of centers at impact and the three rectangular axes. The deductions just made reveal the fact that the electrons of group $(d\lambda)$, upon collision with metal atoms, become members of other groups

($d\lambda'$) all having the same total energy as the group ($d\lambda$), the new components of velocity being related to the old ones by equations (6a), (7), (8). This fact in turn leads to a method of calculating the number of reverse collisions by electrons of groups ($d\lambda'$) such that after collision their representative points lie with those of the undeflected electrons of group ($d\lambda$). It follows from expression (5) that the number of *such* reverse collisions by electrons from a group ($d\lambda'$) such that the angle between the line of centers at impact and the direction of the velocity v' is ϑ' is

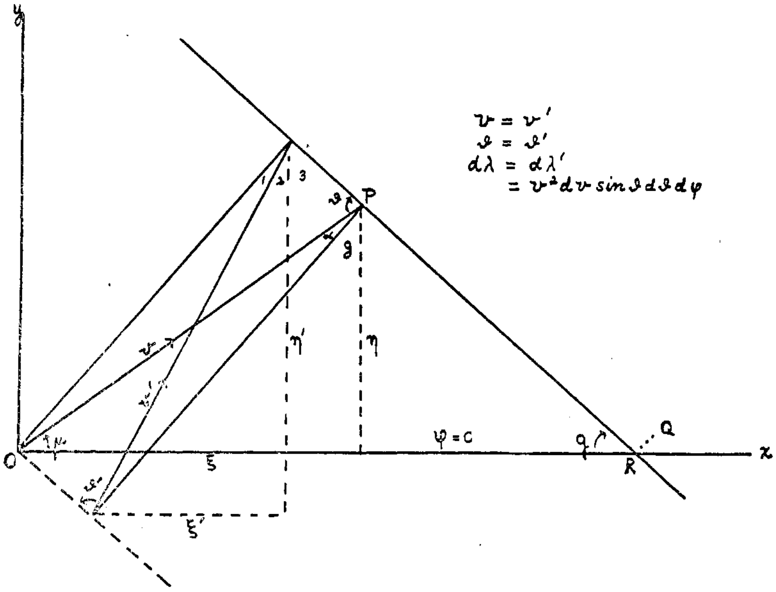

FIG. 2. DIAGRAM OF VELOCITIES

$$n\, R^2 f\,(\xi'\ \eta'\ \zeta')\ d\ \lambda'\ v'\ \cos\vartheta'\ \sin\vartheta'\ d\vartheta'\ d\varphi \qquad (9)$$

$$(v' = v;\ \vartheta' = \vartheta;\ d\lambda' = d\lambda)$$

where the values of ξ', η', ζ' depend upon the orientation of the line of centers at impact. Hence,

$$b - a = n\, R^2\, v \int_0^{\pi/2} \int_0^{2\pi} [f\,(\xi', \eta', \zeta') - f\,(\xi, \eta, \zeta)] \cos\vartheta \sin\vartheta\, d\vartheta\, d\varphi \qquad (10)$$

and from equation (4),

$$n R^2 v \int_0^{\pi/2} \int_0^{2\pi} [f\,(\xi'\,\eta'\,\zeta') - f\,(\xi\,\eta\,\zeta)] \cos\vartheta \,\sin\vartheta \; d\vartheta \; d\varphi = X \frac{\partial f}{\partial \xi} + \xi \frac{\partial f}{\partial x} \quad (11)$$

A solution of the equation, in the form

$$f = f_0 + \xi\,\chi\,(v) \quad (12)$$

is to be tried, where f_0 is the normal distribution function and $\chi(v)$ an unknown function of the velocity alone. Substitution in (11) gives:

$$n R^2 v \chi\,(v) \int_0^{\pi/2} \int_0^{2\pi} (\xi' - \xi) \cos\vartheta \sin\vartheta \, d\vartheta \, d\varphi = X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \quad (13)$$

On the right-hand side of the preceding equation f_0 is used instead of the more exact $f_0 + \xi\chi(v)$. This procedure is permissible as an approximation, on account of the form of the expression and of the fact that f_0 is large in comparison with its perturbation. Obviously this approximation would be useless on the left-hand side of the equation. Substitution of the value of $(\xi' - \xi)$ from equation (6a) gives:

$$-\,2\, n R^2 v^2 \chi\,(v) \int_0^{\pi/2} \int_0^{2\pi} \cos g \, \cos^2\vartheta \, \sin\vartheta \; d\vartheta \; d\varphi = X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \quad (14)$$

The line of centers at impact (PR...Q in figure 1) and the axis Ox are not necessarily in the same plane; g is the angle between these two lines. Ox is inclined to the line OP (the direction of v) at an angle μ. The line of centers is inclined to OP at an angle ϑ. φ is the dihedral angle between the plane (PR...Q and OP) and the plane of (Ox and OP); whence,

$$\cos g = \cos\mu \, \cos\vartheta + \sin\mu \, \sin\vartheta \, \cos\varphi \quad (15)$$

$$\left(\cos\mu = \frac{\xi}{v}\right).$$

Substitution in equation (14) gives:

$$-\,2\, n R^2 v^2 \chi\,(v) \int_0^{\pi/2} \int_0^{2\pi} (\cos\mu \, \cos\vartheta + \sin\mu \, \sin\vartheta \, \cos\varphi) \cos^2\vartheta \, \sin\vartheta \; d\vartheta \; d\varphi \quad (16)$$

The result of integration with respect to φ is:

$$-4\pi n R^2 v \chi(v) \xi \int_0^{\pi/2} \cos^3\vartheta \sin\vartheta \, d\vartheta = X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \tag{17}$$

integration with respect to ϑ gives:

$$-\pi n R^2 v \chi(v) \xi = X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \tag{18}$$

The unknown function $\chi(v)$ is thus found to be:

$$\chi(v) = \frac{-l}{v \xi} \left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \right) \tag{18a}$$

in which l has been set equal to $\dfrac{1}{\pi n R^2}$. The essayed solution in which χ is assumed to depend upon v alone is thus found to be satisfactory since ξ itself disappears from the right-hand side of equation (18a) upon performing the indicated operations,

$$\left[\frac{1}{\xi} \frac{\partial}{\partial \xi} = \frac{1}{v} \frac{\partial}{\partial v} \right].$$

Hence, the distribution function describing the system is

$$f = f_0 - \frac{l}{v} \left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \right) \tag{19}$$

and by equation (2), the quantity of electricity J transported per second per unit cross-section is:

$$J = e \int \xi \left[f_0 - \frac{l}{v} \left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \right) \right] d\lambda \tag{20}$$

and by equation (1)

$$J = -e \int \frac{\xi l}{v} \left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \right) d\lambda \tag{21}$$

The quantity of heat W transported per second per unit cross-section is, similarly,

$$W = \frac{m}{2}\int v^2 \xi \left[f_0 - \frac{l}{v}\left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \right) \right] d\lambda = -\frac{m}{2}\int \xi l v \left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \right) d\lambda \quad (21a)$$

II. APPLICATION OF CLASSICAL STATISTICS TO THE PROBLEM OF CONDUCTION

In so far as the assumptions and approximations of the last section, which constitutes essentially the treatment of Lorentz, are adequate to describe the phenomenon of conduction in metals, there remains only the choice of a normal distribution function f_0 and its application to formulas (21) and (21a) in order to obtain a final solution of the problem. The classical distribution function of Maxwell and Boltzmann was used by Lorentz and is easily obtained by commencing with the relationship accredited to Boltzmann connecting the entropy of a system with its thermodynamic probability. The latter quantity is defined as the number of microscopic complexions in a given collection all of which correspond to the same macroscopic state of the system. A given microscopic complexion is specified by means of the position coördinates and corresponding components of momenta of each of the molecules of the system. Varying numbers of microscopic complexions thus correspond with various macroscopic states, there being the maximum number of microscopic complexions in the equilibrium macroscopic state. The various microscopic complexions corresponding with a given macroscopic state differ by permutations of the individual molecules, the individuality of the molecules being insignificant as regards the macroscopic state. Boltzmann's relationship is

$$S = k \log W \quad (22)$$

where S is the entropy, k a proportionality constant to be identified later, and W the thermodynamic probability corresponding with the state of the system giving rise to the entropy S. In order to specify the positions and momenta of the molecules it is convenient to conceive a space of six dimensions, along three of the axes of which the space coördinates of the molecules are represented, and along the other three axes of which the coördinates of momenta are represented. This six-dimensional space (the phase-space) is divided into cells of equal magnitude; the magnitude of a cell is small in comparison with the entire space representing the system. A macroscopic state of a system is thus specified by N_1 molecules having representative points lying in cell 1, N_2 molecules in cell 2, ... N_s molecules in cell s. The number of ways in which this distribution can be realized by a system containing N molecules is:

$$W = \frac{N\,!}{N_1\,!\,N_2\,!\,.\,.\,.\,.\,N_s\,!}; \tag{23}$$

$$\sum_s N_s = N \tag{24}$$

The total energy E is accordingly:

$$E = \sum_s \epsilon_s N_s$$

where $\epsilon_1, \epsilon_2, \ldots \epsilon_s$ are the energies characteristic of the cells 1, 2, . . . s, and the summations are taken so as to include all of the cells of the phase-space. If the distribution is an equilibrium one, then it gives rise to the maximum entropy; or

$$\frac{1}{k}\,\delta S = \delta \log W = 0 \tag{25}$$

for *any* arbitrary, small variation in the equilibrium. If the system contains a constant number of molecules and a constant energy, it follows that

$$\delta N = \sum_s \delta N_s = 0 \tag{26}$$

$$\delta E = \sum_s \epsilon_s\,\delta N_s = 0 \tag{27}$$

as subsidiary conditions on the arbitrary variation in the equilibrium. By an application of Stirling's formula,

$$\log x\,! = x \log x - x,$$

it follows from equation (23) that:

$$\log W = N \log N - N - \sum_s N_s \log N_s + \sum_s N_s \tag{28}$$

and

$$\delta \log W = - \sum_s (\log N_s + 1)\, \delta N_s = 0 \tag{29}$$

The subsidiary conditions, $\delta N = 0$ and $\delta E = 0$, rob two of the δN's of their independence. Thus any variation, subject to the imposed conditions, involves at least three cells:

$$-\frac{1}{k}\delta S = (\log N_1 + 1)\,\delta N_1 + (\log N_2 + 1)\,\delta N_2 + (\log N_3 + 1)\,\delta N_3 = 0 \tag{30}$$

$$\delta N = \delta N_1 + \delta N_2 + \delta N_3 = 0 \tag{31}$$

$$\delta E = \epsilon_1 \delta N_1 + \epsilon_2 \delta N_2 + \epsilon_3 \delta N_3 = 0 \tag{32}$$

These equations may be solved by finding quantities α and β by which equations (31) and (32) respectively are to be multiplied, such that upon addition of the three equations the coefficients of δN_1 and δN_2 vanish. Then

$$(\log N_3 + 1 + \alpha + \beta\, \epsilon_3)\, \delta N_3 = 0$$

and since

$$\delta N_3 \neq 0$$

$$(\log N_3 + 1 + \alpha + \beta\, \epsilon_3 = 0$$

$$N_3 = e^{-1-\alpha-\beta\epsilon_3} = A\, e^{-\beta\epsilon_3}$$

where A is a constant.

If cells 2, 3, and s are now chosen for the arbitrary variation, with the same multipliers α and β, the coefficients of δN_2 and δN_3 vanish, and hence that of δN_s; or

$$N_s = A\, e^{-\beta\epsilon_s} \tag{33}$$

The constants α and β can be determined from a formal comparison of thermodynamic quantities with the equations themselves:

$$\begin{cases} -\frac{1}{k}\,\delta S = 0 \\ \alpha\,\delta N = 0 \\ \beta\,\delta E = 0 \end{cases}$$

$$\frac{1}{k}\,\delta S - \alpha\,\delta N - \beta\,\delta E = 0$$

If partial differential coefficients, at constant volume, are formed, it follows that:

$$\frac{1}{k}\left(\frac{\partial S}{\partial E}\right)_{V,N} = \beta; \tag{34}$$

$$\frac{1}{k}\left(\frac{\partial S}{\partial N}\right)_{E,V} = \alpha \tag{35}$$

From the definition of the change in entropy of a given quantity of matter:

$$dS = \frac{dE + p\,dV}{T} \tag{36}$$

where T is the absolute temperature and p the pressure. It follows that

$$\beta = \frac{1}{kT} \tag{37}$$

The coefficient $\left(\frac{\partial S}{\partial N}\right)_{E,V}$ may be found by considering the entropy as a function of the three independent variables E, V, N.

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN \tag{38}$$

By means of (36),

$$dS = \frac{1}{T}\,dE + \frac{p}{T}\,dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN \tag{39}$$

$$\left[\frac{\partial}{\partial N}(TS - E - pV)\right]_{T,\,p} \equiv -\left(\frac{\partial F}{\partial N}\right)_{T,\,p} = T\left(\frac{\partial S}{\partial N}\right)_{E,\,V} = \alpha\, k\, T \quad (40)$$

or

$$\alpha = -\frac{\bar{\zeta}}{k\,T} \quad (41)$$

where ζ is the chemical potential, i.e., the "partial molal" free energy (reckoned per molecule). Had the partial differential coefficients been taken at constant pressure instead of at constant volume, the significance of both α and β would have been altered, but altered in a manner such as not to affect equation (33); for the system of equations (33) determines the maximum entropy, and with constant N, E, and V the entropy, as well as pressure, etc., is fixed.

The following equations serve for the determination of the constants A and k:

$$N = \sum_s N_s = A \sum_s e^{-\beta \epsilon_s} = A \int e^{-\frac{\epsilon}{k\,T}}\, dp_x\, dp_y\, dp_z \quad (42)$$

$$E = \sum_s N_s\, \epsilon_s = A \sum_s \epsilon_s\, e^{-\beta \epsilon_s} = A \int \epsilon\, e^{-\epsilon/k\,T}\, dp_x\, dp_y\, dp_z \quad (43)$$

where p_x, p_y, p_z are components of momentum corresponding with the energy ϵ. If the energy is wholly kinetic,

$$\frac{1}{2}\, m\, v^2 = \epsilon \quad (44)$$

$$m\, v\, dv = d\epsilon \quad (45)$$

$$v^2\, dv = \frac{\sqrt{2}}{m^{3/2}} \sqrt{\epsilon}\, d\epsilon \quad (46)$$

Also

$$dp_x\, dp_y\, dy_z = m^3\, d\xi\, d\eta\, d\zeta = m^3\, v^2\, dv\, \sin\vartheta\, d\vartheta\, d\varphi \quad (47)$$

where ϑ, φ are angles determining the direction of the velocity in spherical polar coördinates.

Whence:

$$N = \sqrt{2}\, A\, m^{3/2} \int_{\epsilon=0}^{\epsilon=\infty} \int_{\vartheta=0}^{\vartheta=\pi} \int_{\varphi=0}^{\varphi=2\pi} e^{-\frac{\epsilon}{kT}} \sqrt{\epsilon}\, d\epsilon \sin\vartheta\, d\vartheta\, d\varphi =$$

$$2^{5/2}\, \pi\, A\, m^{3/2} \int_0^\infty e^{-\frac{\epsilon}{kT}} \sqrt{\epsilon}\, d\epsilon \qquad (48)$$

$$E = \sqrt{2}\, A\, m^{3/2} \int_{\epsilon=0}^{\infty} \int_{\vartheta=0}^{\pi} \int_{\varphi=0}^{2\pi} e^{-\frac{\epsilon}{kT}} \epsilon^{3/2}\, d\epsilon \sin\vartheta\, d\vartheta\, d\varphi =$$

$$2^{5/2}\, \pi\, A\, m^{3/2} \int_0^\infty e^{-\frac{\epsilon}{kT}} \epsilon^{3/2}\, d\epsilon \qquad (49)$$

$$\int_0^\infty e^{-\frac{\epsilon}{kT}} \epsilon^n\, d\epsilon = (k\,T)^{n+1}\, \Gamma\,(n+1)$$

$$\Gamma\,(3/2) = \frac{1}{2}\sqrt{\pi}$$

$$\Gamma\,(5/2) = \frac{3}{4}\sqrt{\pi}$$

$$N = (2\,\pi\, m\, k\, T)^{3/2} A;\; A = \frac{N}{(2\,\pi\, m\, k\, T)^{3/2}} \qquad (50)$$

$$E = \frac{N}{(2\,\pi\, m\, k\, T)^{3/2}} (k\,T)^{5/2} \cdot \frac{3}{2} \cdot (2\,\pi\, m)^{3/2} = \frac{3}{2} N\, k\, T \qquad (51)$$

The heat capacity of the gas,

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = \frac{3}{2} N\, k \qquad (52)$$

Whence by comparison with experiment,

$$k = \frac{R}{N}$$

where R is the molar gas constant.

On the basis of classical statistics, therefore, it follows that the number of molecules having components of momentum lying between p_x and $p_x + dp_x$, p_y and $p_y + dp_y$, p_z and $p_z + dp_z$ is:

$$\frac{N}{(2\,\pi\,m\,k\,T)^{3/2}}\,e^{-\frac{(p_x^2 + p_y^2 + p_z^2)}{2\,m\,k\,T}}\,dp_x\,dp_y\,dp_z \tag{53}$$

where N is the total number of molecules. The number having given velocity components is:

$$N\left(\frac{m}{2\,\pi\,k\,T}\right)^{3/2} e^{-\frac{m}{2\,k\,T}(\xi^2 + \eta^2 + \zeta^2)}\,d\xi\,d\eta\,d\zeta \tag{54}$$

and the number having a velocity of magnitude v is

$$4\,\pi\,N\cdot\left(\frac{m}{2\,\pi\,k\,T}\right)^{3/2} e^{-\frac{m\,v^2}{2\,k\,T}}\,v^2\,dv \tag{55}$$

The distribution function f_0 appropriate for application in equations (21) and (21a) is thus:

$$f_0 = A'\,e^{-b\,v^2}$$

where

$$A' = \frac{N}{V}\left(\frac{m}{2\,\pi\,k\,T}\right)^{3/2} = n\left(\frac{m}{2\,\pi\,k\,T}\right)^{3/2}$$

and

$$b = \frac{m}{2\,k\,T}$$

Equations (21) and (21a) for the quantities of electricity and of heat, respectively, transferred through unit cross-section per second are:

$$J = -\,e\int\frac{\xi\cdot l}{v}\left(X\,\frac{\partial f_0}{\partial\xi} + \xi\,\frac{\partial f_0}{\partial x}\right)d\xi\,d\eta\,d\zeta \tag{21}$$

$$W = -\,\frac{m}{2}\int\xi\cdot l\cdot v\left(X\,\frac{\partial f_0}{\partial\xi} + \xi\,\frac{\partial f_0}{\partial x}\right)d\xi\,d\eta\,d\zeta \tag{21a}$$

$$\frac{\partial f_0}{\partial \xi} = -2A'be^{-bv^2}\xi$$

$$\frac{\partial f_0}{\partial x} = \left[\frac{\partial A'}{\partial x} - A'v^2\frac{\partial b}{\partial x}\right]e^{-bv^2}$$

$$X\frac{\partial f_0}{\partial \xi} + \xi\frac{\partial f_0}{\partial x} = -\xi e^{-bv^2}\left(2A'bX - \frac{\partial A'}{\partial x} + A'v^2\frac{\partial b}{\partial x}\right) \tag{56}$$

Whence

$$J = e \cdot l\int \xi^2 e^{-bv^2}\left(\frac{2A'bX}{v} - \frac{1}{v}\frac{\partial A'}{\partial x} + A'v\frac{\partial b}{\partial x}\right)d\xi\, d\eta\, d\zeta \tag{57}$$

$$W = \frac{m \cdot l}{2}\int \xi^2 e^{-bv^2}\left(2A'bXv - v\frac{\partial A'}{\partial x} + A'v^3\frac{\partial b}{\partial x}\right)d\xi\, d\eta\, d\zeta \tag{57a}$$

ξ^2 may be replaced by $\frac{v^2}{3}$, $d\xi\, d\eta\, d\zeta$ by $4\pi v^2\, dv$, and v^2 by q, whence

$$J = \frac{4\pi e l}{3}\int_0^\infty e^{-bq}\left(A'bXq - \frac{1}{2}\frac{\partial A'}{\partial x}q + \frac{A'}{2}\frac{\partial b}{\partial x}q^2\right)dq \tag{58}$$

$$W = \frac{2\pi l m}{3}\int_0^\infty e^{-bq}\left(A'bXq^2 - \frac{1}{2}\frac{\partial A'}{\partial x}q^2 + \frac{A'}{2}\frac{\partial b}{\partial x}q^3\right)dq \tag{58a}$$

$$\int_0^\infty e^{-bq}q^n\, dq = \frac{n\,!}{b^{n+1}}$$

if n is an integer. Whence

$$J = \frac{4\pi e l}{3}\left(\frac{A'X}{b} - \frac{1}{2b^2}\frac{\partial A'}{\partial x} + \frac{A'}{b^3}\frac{\partial b}{\partial x}\right) \tag{59}$$

$$W = \frac{2\pi l m}{3}\left(\frac{2A'X}{b^2} - \frac{1}{b^3}\frac{\partial A'}{\partial x} + \frac{3A'}{b^4}\frac{\partial b}{\partial x}\right) \tag{59a}$$

The coefficient of electrical conductivity σ, under the condition of constant temperature throughout the conductor $\left(\frac{\partial A'}{\partial x} = 0,\right.$

$\left.\frac{\partial b}{\partial x} = 0\right)$, is easily obtained from equation (59). The acceleration X is given by $\frac{eE}{m}$ where E is the electric intensity. Whence, the value obtained by Lorentz:

$$\sigma = \frac{J}{E} = \frac{4\,\pi}{3}\,\frac{e^2\,l\,A'}{m\,b}$$

$$\frac{A'}{b} = n\left(\frac{m}{2\,\pi\,k\,T}\right)^{3/2} \cdot \frac{2\,k\,T}{m} = \frac{n}{\pi^{3/2}}\sqrt{\frac{m}{2\,k\,T}}$$

$$\sigma = \frac{4}{3}\,\frac{e^2\,l\,n}{\sqrt{2\,\pi\,m\,k\,T}} \tag{60}$$

The coefficient of thermal conductivity in a conductor in which there is no flow of electricity can be obtained from equation (59a) by utilizing the relationship $J = 0$ from equation (59).

$$J = 0 = \frac{4\,\pi}{3}\,e\,l\left(\frac{A'\,X}{b} - \frac{1}{2\,b^2}\,\frac{\partial A'}{\partial x} + \frac{A'}{b^3}\,\frac{\partial b}{\partial x}\right) \tag{61}$$

whence

$$\frac{2\,A'\,X}{b^2} - \frac{1}{b^3}\,\frac{\partial A'}{\partial x} = -\,\frac{2\,A'}{b^4}\,\frac{\partial b}{\partial x} \tag{62}$$

Substitution by means of this equation in equation (59a) gives

$$W = \frac{2\,\pi}{3}\,l\,m\,\frac{A'}{b^4}\,\frac{\partial b}{\partial x} \tag{63}$$

$$\frac{\partial b}{\partial x} = \frac{\partial b}{\partial T}\,\frac{\partial T}{\partial x} = -\,\frac{m}{2\,k\,T^2}\,\frac{\partial T}{\partial x} \tag{64}$$

$$\frac{A'}{b^4} = \frac{n}{\pi^{3/2}}\left(\frac{2\,k\,T}{m}\right)^{5/2}$$

or,

$$W = -\,\frac{8}{3}\,\frac{l\,n\,k^2\,T}{\sqrt{2\,\pi\,m\,k\,T}}\,\frac{\partial T}{\partial x} \tag{65}$$

If the coefficient of thermal conductivity κ is defined by the equation

$$W = -\kappa \frac{\partial T}{\partial x} \tag{66}$$

the value obtained by Lorentz follows from comparison:

$$\kappa = \frac{8}{3} \frac{l\, n\, k^2\, T}{\sqrt{2\, \pi\, m\, k\, T}} \tag{67}$$

and

$$\frac{\kappa}{\sigma} = 2 \left(\frac{k}{e}\right)^2 T = 0.165 \times 10^{-12}\, T.$$

The ratio has the value 4.8×10^{-11} for a temperature of 291°K. Experimental values for the ratio $\frac{\kappa}{\sigma}$ for common metals show a proportionality with T, and at a temperature of 291°K have approximately the value 7×10^{-11}. In the application of formulas such as (60) or (67), the quantity l, which is of the nature of a mean free path, is to be treated as an adjustable constant. For silver, as an example, if the number of free electrons is assumed to be equal to the number of metal atoms, the experimental value of σ (1/1600 in c.g.s. units) in equation (60) leads to a value of l equal to 4.7×10^{-7} cm. The assumption just made regarding the number of free electrons leads, on the basis of classical statistics, to a heat capacity contribution to the metal of $\frac{3}{2}\, Nk$, and even though the heat capacity of the electron-gas of the metal cannot be measured, theoretical evidence concerning the heat capacity of metals points towards a very inconsequential contribution from the electrons. Thus, in accordance with the theory presented, it is necessary, in order to explain satisfactorily the experimental values of σ, to assume that the number of free electrons is approximately equal to the number of metal atoms. This assumption in turn leads to an absurdly large contribution to the heat capacity.

III. APPLICATION OF THE NEW STATISTICS TO THE PROBLEM OF CONDUCTION

In the new systems of statistics, as developed either by Bose and Einstein or by Fermi, the fundamental postulate of Boltzmann relating entropy to thermodynamic probability is retained, but the method of calculating the thermodynamic probability is altered. As in the classical statistics, a phase-space is conceived for describing a system and is divided into cells of equal magnitude h^f, where h is Planck's constant and f the number of degrees of freedom of the molecule. In the development of classical statistics as given in section II of this article, the magnitude of the cells was not specified; nor was it necessary for the application there made. It would have been necessary there, however, had a numerical calculation of the entropy been attempted, but such an attempted calculation would have revealed an inconsistency in the calculation of the thermodynamic probability, forcing an "ad hoc" revision but not affecting the form of the distribution function. Besides removing the inconsistency just mentioned, the new systems of statistics, and especially the system developed by Fermi, appear to have a deeper physical basis than does the classical statistics. The statistics of Bose and Einstein and of Fermi both lead to essentially the same distribution function as classical statistics for gases at high temperatures and low densities. There are marked departures however in the case of gases under conditions such that the ratio of the temperature to the number of molecules per cubic centimeter $\frac{T}{n}$ is comparatively low. A gas in such a state is said to be degenerate. The conception of the free electrons in a metal as a gas and the assumption that the number of free electrons is equal to the number of metal atoms necessitate an extremely large value for n, as compared with gases under ordinary conditions of temperature and pressure; even for comparatively high temperatures, the ratio $\frac{T}{n}$ is so low that the electron-gas is in a highly degenerate state. Hence it is to be expected that the new statistics in its application to the problem of conduction should lead to results very different from those of the classical theory.

According to the new statistics, a given state of a system (corresponding with a region of the phase-space containing Δs cells, all representing the same energy but different positions) is characterized by

$p_0 \, \Delta \, s$ cells being empty

$p_1 \, \Delta \, s$ cells containing one molecule

⋮

$p_r \, \Delta \, s$ cells containing r molecules

$$\Sigma \, p_r = 1$$

The number of ways in which the given distribution can be realized, it being assumed that cells but not molecules have "identity," is:

$$W_{\Delta s} = \frac{\Delta \, s \, !}{(p_0 \, \Delta \, s) \, ! \, (p_1 \, \Delta \, s) \, ! \, \ldots\ldots \, (p_r \, \Delta \, s) \, !} \tag{69}$$

and $W_{\Delta s}$ is interpreted as the thermodynamic probability corresponding with the selected region of the phase-space. By Stirling's formula:

$$\begin{aligned} \log W_{\Delta s} &= \Delta \, s \log \Delta \, s - \Delta \, s - \sum_r p_r \, \Delta \, s \log (p_r \, \Delta \, s) + \Sigma \, p_r \, \Delta \, s \\ &= \Delta \, s \log \Delta \, s - \Delta \, s \sum_r p_r \log p_r - \Delta \, s \log \Delta \, s \\ &= - \Delta \, s \sum_r p_r \log p_r \end{aligned} \tag{70}$$

The logarithm of the probability per cell in the $\Delta \, s$-region is therefore

$$- \sum_r p_r \log p_r,$$

and the entropy of the entire system is

$$S = k \log W = - k \sum_s \sum_r p_r^s \log p_r^s \tag{71}$$

The summation with respect to r, according to the statistics of Bose and Einstein, runs from $r = 0$ to $r = \infty$ and, according to the statistics of Fermi, from $r = 0$ to $r = 1$, (i.e., a cell is either empty or contains one molecule). The summation with respect to s includes all cells of the phase-space of the system, compatible with its energy and volume. The quantities p_r^s etc. are to be interpreted as the probability that the s^{th} cell contains r molecules, etc., in the sense that $\sum_r p_r^s r$ gives the average number of molecules in the s^{th} cell, $\sum_r p_r^{s+1} r$ the average number in the $(s + 1)^{\text{th}}$ cell, etc.

In order to find the equilibrium distribution of a given system, it is necessary to render the entropy S a maximum, subject to the conditions of a constant number of molecules and constant energy. In accordance with the preceding notation the total number of molecules and the total energy are respectively:

$$N = \sum_s N_s = \sum_s \sum_r p_r^s \, r \tag{72}$$

$$E = \sum_s N_s \epsilon_s = \sum_s \sum_r \epsilon_s \, p_r^s \, r \tag{73}$$

where $\epsilon_1, \epsilon_2, \ldots \epsilon_s$ are the energies characteristic of the cells $1, 2 \ldots s$. The entropy is rendered a maximum by setting δS equal to zero for *any*, arbitrary, small variation of the quantities governing the distribution; i.e.,

$$-\frac{1}{k} \, \delta \, S = - \, \delta \log W = \sum_s \sum_r (\log p_r^s + 1) \, \delta \, p_r^s = 0 \tag{74}$$

Likewise, in order that N and E be constants during the variation:

$$\delta N = \sum_s \delta \, N_s = \sum_s \sum_r r \, \delta \, p_r^s = 0 \tag{75}$$

$$\delta \, E = \sum_s \epsilon_s \, \delta \, N_s = \sum_s \sum_r \epsilon_s \, r \, \delta \, p_r^s = 0 \tag{76}$$

and further, since

$$\sum_r p_r^s = 1$$

$$\sum_s \sum_r \delta\, p_r^s = 0 \tag{77}$$

With three subsidiary equations restricting the general variation, three δp's are robbed of their independence, and hence *any* variation, subject to the imposed conditions, involves at least four p's. By an application of an exactly similar method as that used for the corresponding problem in the classical statistics; i.e., by finding quantities α, β, γ by which equations (75), (76), (77) respectively are to be multiplied, such that upon addition of the four equations, (74) (75) (76) (77), the coefficients of three of the four δp's vanish, it follows that, since the fourth δp cannot be zero, its coefficient must vanish, or

$$p_r^s = e^{-1-\gamma_s-(\alpha+\beta\epsilon_s)r} \tag{78}$$

The constant γ (requiring a subscript) can be determined at once from the relationship:

$$\sum_r p_r^s = 1 = e^{-1-\gamma_s} \sum_r e^{-(\alpha+\beta\epsilon_s)r} \tag{79}$$

$$e^{-1-\gamma_s} = \frac{1}{\sum\limits_r e^{-(\alpha+\beta\epsilon_s)r}} \tag{80}$$

In the statistics of Bose and Einstein, $r = 0, 1, \ldots . \infty$, whence,

$$e^{-1-\gamma_s} = 1 - e^{-(\alpha+\beta\epsilon_s)} \tag{81}$$

and in the statistics of Fermi, $r = 0, 1$, whence,

$$e^{-1-\gamma_s} = \frac{1}{1+e^{-(\alpha+\beta\epsilon_s)}} \tag{82}$$

The constants α, β, by reference to equations (41) and (37) and to their mode of introduction in equations (75) and (76) are recognized respectively as $-\frac{\bar{\zeta}}{kT}$ and $\frac{1}{kT}$. For a pure gas, the free energy ($F = N\bar{\zeta}$) is thus

$$F = E + pV - TS = -NkT\alpha \tag{83}$$

The number of molecules in any cell s is, according to the statistics of Bose and Einstein, found from equations (72), (78) and (81) to be:

$$N_s = \sum_{r=0}^{r=\infty} p_r^s\, r = \left[1 - e^{-(\alpha + \beta \epsilon_s)}\right] \sum_r r\, e^{-(\alpha + \beta \epsilon_s) r} = \frac{1}{e^{\alpha + \beta \epsilon_s} - 1} \tag{84}$$

and, according to the statistics of Fermi, from equations (72), (78) and (82):

$$N_s = \sum_{r=0}^{r=1} p_r^s\, r = \left[\frac{1}{1 + e^{-(\alpha + \beta \epsilon_s)}}\right] \sum_{0,1} r\, e^{-(\alpha + \beta \epsilon_s) r} = \frac{1}{e^{\alpha + \beta \epsilon_s} + 1} \tag{85}$$

The total number of molecules and the total energy are respectively:

$$N = \Sigma N_s = \sum_s \frac{1}{e^{\alpha + \beta \epsilon_s} \mp 1} \tag{86}$$

$$E = \Sigma N_s \epsilon_s = \sum_s \frac{\epsilon_s}{e^{\alpha + \beta \epsilon_s} \mp 1} \tag{87}$$

From equations (71) and (78), it follows that the entropy is:

$$S = -k \sum_s \sum_r p_r^s \left[-\alpha r - \beta \epsilon_s r \pm \log\left(1 \mp e^{-(\alpha + \beta \epsilon_s)}\right)\right] \tag{88}$$

where, in the cases of alternation in sign, the upper sign is to be read for the statistics of Bose and Einstein and the lower one for the statistics of Fermi.

$$\sum_s \sum_r p_r^s\, r\, \alpha = N \alpha; \quad \sum_s \sum_r p_r^s\, \epsilon_s\, r\, \beta = \beta E$$

whence

$$S = N k \alpha + k \beta E \mp k \sum_s \log\left(1 \mp e^{-(\alpha + \beta \epsilon_s)}\right) \tag{89}$$

and since

$$F = -N k T \alpha, \quad \beta = \frac{1}{k T},$$

it follows that

$$S = -\frac{F}{T} + \frac{E}{T} \mp k \sum_s \log\left(1 \mp e^{-(\alpha + \beta \epsilon_s)}\right) \tag{90}$$

By reference to the thermodynamic definition of F, it follows that

$$\frac{p\,V}{T} = \mp k \sum_s \log\left(1 \mp e^{-\alpha - \beta \epsilon_s}\right) \tag{91}$$

It is immediately evident from equation (85) that, if the gas is in a state such that

$$e^{\alpha} = \frac{1}{A} \gg 1,$$

the distribution function of Bose and Einstein, or of Fermi, becomes essentially $A\ e^{-\beta \epsilon_s}$

$$(A\, \Sigma\, e^{-\beta \epsilon_s} = \Sigma\, N_s = N) \tag{92}$$

and is therefore as regards form in accord with the classical theory. Furthermore, with the condition that $e^{\alpha} \gg 1$,

$$\frac{p\,V}{k\,T} = \mp \sum_s \log\left(1 \mp e^{-\alpha - \beta \epsilon_s}\right) \cong \mp \sum_s \mp e^{-\alpha - \beta \epsilon_s} = \sum_s A\, e^{-\beta \epsilon_s} = N \tag{93}$$

and by comparison with the experimental equation $pV = RT$, k is identified with $\frac{R}{N}$, R being the molar gas constant.

The constant $A (= e^{-\alpha})$ can be determined from equation (92) by replacing the sum by the corresponding integral:

$$\sum_s A\, e^{-\beta \epsilon_s} = A \int \cdots \int e^{-\beta \epsilon}\, \frac{dp_x\, dp_y\, dp_z\, dx\, dy\, dz}{h^3} \tag{94}$$

The magnitude of a cell in the phase-space is thus assumed to be sufficiently small that for the purpose of integration it may be identified with $dp_x dp_y dp_z dx dy dz$. The integrations extend over all values of p_x, p_y, p_z consistent with the energy and over all values of x, y, z consistent with the volume. As in equations (44) etc.,

$$\int\int\int dx\,dy\,dz = \int dV = V$$

$$dp_x\,dp_y\,dp_z = m^3\,d\xi\,d\eta\,d\zeta = m^3\,v^2\,d\,v\,\sin\vartheta\,d\vartheta\,d\varphi = m^{3/2}\sqrt{2\,\epsilon}\,d\epsilon\,\sin\vartheta\,d\vartheta\,d\varphi$$

$$m^{3/2}\sqrt{2\,\epsilon}\,d\epsilon\int_{\vartheta\,=\,0}^{\vartheta\,=\,\pi}\int_{\varphi\,=\,0}^{\varphi\,=\,2\pi}\sin\vartheta\,d\vartheta\,d\varphi = 2^{5/2}\,\pi\,m^{3/2}\sqrt{\epsilon}\,d\epsilon$$

whence from equation (94),

$$N = \frac{A\cdot 2^{5/2}\,\pi\,V\,m^{3/2}}{h^3}\int_0^\infty e^{-\frac{\epsilon}{k\,T}}\sqrt{\epsilon}\,d\epsilon = \frac{(2\,\pi\,m\,k\,T)^{3/2}\,A\,V}{h^3} \qquad (95)$$

it being legitimate to extend the upper limit to ∞ on account of the form of the function. It follows that

$$A = \frac{N}{V}\frac{h^3}{(2\,\pi\,m\,k\,T)^{3/2}} = n\cdot\frac{h^3}{(2\,\pi\,m\,k\,T)^{3/2}} \qquad (96)$$

The condition of non-degeneracy (i.e., $e^\alpha = \frac{1}{A} \gg 1$), in which case the form of the new distribution function does not differ essentially from the classical, is therefore that

$$\frac{n\,h^3}{(2\,\pi\,m\,k\,T)^{3/2}} \ll 1 \qquad (97)$$

For helium gas at 273°K and one atmosphere pressure

$$A \cong 4\times 10^{-6} \ll 1\left(\begin{array}{l} n = \dfrac{6.06\times 10^{23}}{22{,}400} \\ m = \dfrac{4}{6.06\times 10^{23}} \end{array}\right)$$

while for the free electrons in silver at 300°K

$$A \cong 0.5\times 10^{4} \gg 1\left(\begin{array}{l} n = \dfrac{d}{M}\times 6.06\times 10^{23} \\ m = 9.02\times 10^{-28} \end{array}\right)$$

Accordingly, the free energy of a non-degenerate gas by equation (83) is:

$$F = -N\,k\,T\,\alpha = N\,k\,T\log A = N\,k\,T\log\left[\frac{N}{V}\,\frac{h^3}{(2\,\pi\,m\,k\,T)^{3/2}}\right] \qquad (98)$$

$$V = \frac{N\,k\,T}{p}$$

whence, the entropy of a non-degenerate gas is:

$$S = -\left(\frac{\partial F}{\partial T}\right)_p = N\,k\log\left[\frac{(2\,\pi\,m\,k\,T)^{3/2}\,e^{5/2}\,V}{N\,h^3}\right] \qquad (99)$$

This theoretical value for the entropy of a monatomic gas corresponds closely with experimental results (based on the third law of thermodynamics) and has been obtained by a variety of theoretical methods.

In the case of a degenerate gas (i.e., one for which $e^{-\alpha} = A >> 1$) equation (94) can no longer be used for the evaluation of A, but rather the exact equation (86) from which equation (94) was evolved:

$$N = \sum_s \frac{1}{e^{\alpha+\beta\epsilon_s}+1} + \frac{2^{5/2}\,\pi\,V\,m^{3/2}}{h^3}\int_0^\infty \frac{\epsilon^{1/2}\,d\epsilon}{\frac{1}{A}e^{\epsilon/k\,T}+1} =$$

$$\frac{2^{5/2}\,\pi\,V\,(m\,k\,T)^{3/2}}{h^3}\int_0^\infty \frac{u^{1/2}\,du}{\frac{1}{A}e^{u}+1} \qquad (100)$$

where u is written for $\frac{\epsilon}{kT}$, and the minus sign corresponding with the assumption of Bose and Einstein is omitted, its significance becoming indefinite for very great values of A. The corresponding integrals for E and pV are:

$$E = \frac{2^{5/2}\,\pi\,V\,k\,T\,(m\,k\,T)^{3/2}}{h^3}\int_0^\infty \frac{u^{3/2}\,du}{\frac{1}{A}e^{u}+1} \qquad (101)$$

$$p\,V = \frac{2^{5/2}\,\pi\,V\,k\,T\,(m\,k\,T)^{3/2}}{h^3}\int_0^{\infty}\log\,(1 + A\,e^{-u})\,u^{1/2}\,du \tag{102}$$

Integration of equation (102) by parts gives:

$$p\,V = \frac{2}{3}\cdot\frac{2^{5/2}\,\pi\,V\,k\,T\,(m\,k\,T)^{3/2}}{h^3}\int_0^{\infty}\frac{u^{3/2}\,du}{\frac{1}{A}e^{u} + 1} = \frac{2}{3}E \tag{103}$$

The generalized integral corresponding with equations (100), (101), etc., is:

$$U_\rho = \frac{1}{\Gamma\,(\rho + 1)}\int_0^{\infty}\frac{u^{\rho}\,du}{\frac{1}{A}e^{u} + 1} \tag{104}$$

where $\rho = 1/2$, $3/2$ etc., and the gamma function of $(\rho + 1)$ dividing the expression serves only in the definition of U_ρ; e.g.,

$$N = \frac{2^{5/2}\,\pi\,V\,(m\,k\,T)^{3/2}}{h^3}\cdot U_{\frac{1}{2}}\cdot\Gamma\left(\frac{1}{2} + 1\right).$$

Sommerfeld has shown that the asymptotic value of U_ρ as $A \rightarrow \infty$ (i.e., $A = A_0$) is:

$$\frac{(\log A_0\,)^{\rho + 1}}{\Gamma\,(\rho + 2)} \tag{105}$$

whence, to first approximations, for very large values of A:

$$N = \frac{2^{5/2}\,\pi\,V\,(m\,k\,T)^{3/2}}{h^3}\,\frac{\Gamma\,(3/2)}{\Gamma\,(5/2)}\,(\log A)^{3/2} = \frac{4\,\pi\,V}{3\,h^3}\,(2\,m\,k\,T)^{3/2}\,(\log A)^{3/2} \tag{106}$$

$$E = \frac{2^{5/2}\,\pi\,V\,k\,T\,(m\,k\,T)^{3/2}}{h^3}\,\frac{\Gamma\,(5/2)}{\Gamma\,(7/2)}\,(\log A)^{5/2} = \frac{4\,\pi\,V\,k\,T}{5\,h^3}\,(2\,m\,k\,T)^{3/2}\,(\log A)^{5/2} \tag{107}$$

Equation (106) gives the value of log A, or more properly log A_0, in terms of measurable quantities:

$$\log A_0 = \left(\frac{3\,n}{4\,\pi}\right)^{2/3}\frac{h^2}{2\,m\,k\,T'}\;\left(n = \frac{N}{V}\right) \tag{108}$$

Substitution of this value in equation (107) gives for the value of the energy of a highly-degenerate gas:

$$E_0 = \left(\frac{3\,n}{4\,\pi}\right)^{5/3} \frac{2\,\pi\,V\,h^2}{5\,m} \tag{109}$$

Sommerfeld has shown that to a second approximation:

$$\log A = \log A_0 \left[1 - \frac{(2\,\pi\,m\,k\,T)^2}{12\,h^4} \left(\frac{3\,n}{4\,\pi}\right)^{-\frac{4}{3}}\right] \tag{110}$$

and

$$E = E_0 \left[1 + \frac{5}{12} \left(\frac{2\,\pi\,m\,k\,T}{h^2}\right)^2 \left(\frac{3\,n}{4\,\pi}\right)^{-\frac{4}{3}}\right] \tag{111}$$

E_0 is the so-called "Nullpunktsenergie" (independent of T); the corresponding "Nullpunktsdruck" is

$$p_0 = \frac{2}{3}\frac{E_0}{V} = \frac{4\,\pi\,h^2}{15\,m}\left(\frac{3\,n}{4\,\pi}\right)^{5/3} \tag{112}$$

The "Nullpunktsentropie" is directly obtained from equation (89):

$$S_0 = N\,k\,\alpha_0 + k\,\beta\,E_0 + k \sum_s \log\left(1 + e^{-\alpha_0 - \beta\epsilon_s}\right)$$

$$\left[\alpha_0 = -\log A_0;\ \beta = \frac{1}{k\,T};\ k \sum_s \log\left(1 + e^{-\alpha_0 - \beta\epsilon_s}\right) = \frac{p_0\,V}{T} = \frac{2}{3}\frac{E_0}{T}\right]$$

whence

$$S_0 = N\,k\left[-\log A_0 + \frac{5}{3}\frac{E_0}{N\,k\,T}\right] \tag{113}$$

From equations (100), (101), (104), (105),

$$\frac{5}{3}\frac{E_0}{N\,k\,T} = \frac{5}{3}\frac{\Gamma(5/2)}{\Gamma(3/2)}\frac{U_{3/2}}{U_{1/2}} = \frac{5}{3}\frac{\Gamma(5/2)\,\Gamma(5/2)}{\Gamma(3/2)\,\Gamma(7/2)}\frac{(\log A_0)^{5/2}}{(\log A_0)^{3/2}} = \log A_0$$

$$[\Gamma\,(1/2) = \sqrt{\pi};\ \Gamma\,(x + 1) = x\,\Gamma\,(x),\ \text{if}\ x > 0]$$

$$S_0 = 0$$

In the development of the statistics of (rotationless) monatomic gases just given, the statistical weight (or *a priori* probability) of each infinitesimal region of the phase-space is postulated to be equal to the extension in phase-space divided by the constant h^3, i.e.,

$$\frac{dp_x\,dp_y\,dp_z\,dx\,dy\,dz}{h^3}$$

This corresponds with the assignment of a statistical weight equal to unity for each mechanically possible stationary state of a ("non-degenerate") quantized system.

Current theories regarding the electron assign to it a spin. This consideration requires that its statistical weight be twice that of a rotationless mass-point, i.e.,

$$\frac{G}{h^3}\,dp_x\,dp_y\,dp_z\,dx\,dy\,dz,\ (G = 2)$$

Thus, in the application of the preceding formulas to electrons, in every instance $\frac{1}{h}$ is replaced by $\frac{G^{\frac{1}{3}}}{h}$. The following list of altered and extended formulas is given for convenience in the subsequent deductions.[1]

$$\frac{N}{V} = \frac{2^{5/2}\,\pi\,G\,(m\,k\,T)^{3/2}}{h^3}\int_0^\infty f_0\,u^{1/2}\,du;\ \left(f_0 = \frac{1}{\frac{1}{A}\,e^u + 1}\right) \tag{114}$$

$$U_\rho = \frac{1}{\Gamma\,(\rho + 1)}\int_0^\infty f_0\,u^\rho\,du \tag{115}$$

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[1] In the case of a non-degenerate gas, it is evident that $f_0 = \frac{1}{\frac{1}{A}\,e^u + 1}$ becomes essentially $A\,e^{-u}$, as in the Lorentz application of the classical statistics. See Sommerfeld's derivation of the Lorentz formulas, Z. Physik **47**, 23, 26 (1928).

To a second approximation:

$$U_0 = \log A \tag{116}$$

$$U_1 = \frac{(\log A)^2}{2\,!}\left[1 + \frac{\pi^2}{3\,(\log A)^2}\right] \tag{117}$$

$$U_2 = \frac{(\log A)^3}{3\,!}\left[1 + \frac{\pi^2}{(\log A)^2}\right] \tag{118}$$

$$\log A = \frac{h^2}{2\,m\,k\,T}\left(\frac{3\,n}{4\,\pi\,G}\right)^{2/3}\left[1 - \frac{1}{12}\left(\frac{2\,\pi\,m\,k\,T}{h^2}\right)^2\left(\frac{3\,n}{4\,\pi\,G}\right)^{-\frac{4}{3}}\right] \tag{119}$$

From equation (111), with the proper insertion of G,

$$E = \frac{2\,\pi}{5}\,\frac{V\,G\,h^2}{m}\left(\frac{3\,n}{4\,\pi\,G}\right)^{5/3}\left[1 + \frac{5}{12}\,\frac{(2\,\pi\,m\,k\,T)^2}{h^4}\left(\frac{3\,n}{4\,\pi\,G}\right)^{-\frac{4}{3}}\right] \tag{120}$$

Whence the heat capacity of the electron-gas is

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = \frac{4\,\pi^3\,m\,G\,V\,k^2\,T}{3\,h^2}\left(\frac{3\,n}{4\,\pi\,G}\right)^{1/3} \tag{121}$$

a quantity which is negligibly small for metals at ordinary temperatures.

With the Fermi distribution function [f_0 of equation (114)], equations (21) and (21a) for the electric current per unit cross-section and the quantity of heat transported per second per unit cross-section, become respectively:

$$J = -\,e\,l\int\frac{\xi}{v}\left(X\,\frac{\partial f_0}{\partial\,\xi} + \xi\,\frac{\partial f_0}{\partial\,x}\right)d\Omega \tag{122}$$

$$W = -\,\frac{m\,l}{2}\int\xi\,v\left(X\,\frac{\partial f_0}{\partial\,\xi} + \xi\,\frac{\partial f_0}{\partial\,x}\right)d\Omega \tag{122a}$$

where

$$d\Omega = 4\,\pi\,G\left(\frac{m}{h}\right)^3 v^2\,dv = B\,v^2\,dv \tag{123}$$

$$\frac{1}{\xi}\frac{\partial f_0}{\partial \xi} = \frac{1}{v}\frac{\partial f_0}{\partial v}; \quad [v^2 = \xi^2 + \eta^2 + \zeta^2]; \quad \xi^2 = \frac{1}{3}v^2$$

Whence

$$J = -\frac{e\,l\,B}{3}\left\{X\int \frac{\partial f_0}{\partial v}\,v^2\,dv + \frac{\partial}{\partial x}\int v^3 f_0\,dv\right\} \tag{124}$$

$$W = -\frac{m\,l\,B}{6}\left\{X\int \frac{\partial f_0}{\partial v}\,v^4\,dv + \frac{\partial}{\partial x}\int v^5 f_0\,dv\right\} \tag{124a}$$

By a change of variable, $u = \dfrac{m\,v^2}{2\,k\,T}$, the equations become:

$$J = -\frac{e\,l\,B}{3}\left\{\frac{2\,k\,T\,X}{m}\int u\,\frac{\partial f_0}{\partial u}\,du + \frac{\partial}{\partial x}\left[2\left(\frac{k\,T}{m}\right)^2\int f_0\,u\,du\right]\right\} \tag{125}$$

$$W = -\frac{m\,l\,B}{6}\left\{\left(\frac{2\,k\,T}{m}\right)^2 X\int u^2\,\frac{\partial f_0}{\partial u}\,du + \frac{\partial}{\partial x}\left[4\left(\frac{k\,T}{m}\right)^3\int f_0\,u^2\,du\right]\right\} \tag{125a}$$

Integration by parts of the first terms on the right gives:

$$J = \frac{e\,l\,B}{3}\left\{\frac{2\,k\,T\,X}{m}\int f_0\,du - \frac{\partial}{\partial x}\left[2\left(\frac{k\,T}{m}\right)^2\int f_0\,u\,du\right]\right\} \tag{126}$$

$$W = \frac{m\,l\,B}{6}\left\{8\left(\frac{k\,T}{m}\right)^2 X\int f_0\,u\,du - \frac{\partial}{\partial x}\left[4\left(\frac{k\,T}{m}\right)^3\int f_0\,u^2\,du\right]\right\} \tag{126a}$$

These integrals correspond with the generalized integral of equation (115) with ρ having the values 0, 1, 2.

Whence

$$J = \frac{2\,e\,l\,B}{3}\left\{\frac{k\,T\,X}{m}\,U_0 - \frac{\partial}{\partial x}\left[\left(\frac{k\,T}{m}\right)^2 U_1\right]\right\} \tag{127}$$

$$W = \frac{4\,m\,l\,B}{3}\left\{\left(\frac{k\,T}{m}\right)^2 X\,U_1 - \frac{\partial}{\partial x}\left[\left(\frac{k\,T}{m}\right)^3 U_2\right]\right\} \tag{127a}$$

For the case of electrical conductivity in a conductor at constant temperature,

$$\left[\frac{\partial T}{\partial x} = 0, \frac{\partial U_1}{\partial x} = \frac{\partial U_1}{\partial T}\frac{\partial T}{\partial x} = 0\right]$$

and with the acceleration X given by $\frac{e\,E}{m}$, where E is the electric intensity, it follows that the coefficient of electrical conductivity is:

$$\sigma = \frac{J}{E} = \frac{2}{3} \cdot \frac{e^2\,l\,k\,T}{m^2}\,B\,U_0 \tag{128}$$

Substitution from equations (123), (116), and (119), the first approximation for log A being used, ($G = 2$), gives:

$$\sigma = \frac{8\,\pi}{3}\frac{e^2\,l}{h}\left(\frac{3\,n}{8\,\pi}\right)^{2/3} \tag{129}$$

In the case of a thermal conductor in which there is no electrical current:

$$J = 0 = \frac{2\,e\,l\,B}{3}\left\{\frac{k\,T\,X\,U_0}{m} - \frac{\partial}{\partial x}\left[\left(\frac{k\,T}{m}\right)^2 U_1\right]\right\} \tag{130}$$

and

$$X = \frac{m}{k\,T\,U_0}\frac{\partial}{\partial x}\left[\left(\frac{k\,T}{m}\right)^2 U_1\right] \tag{131}$$

Whence, by substitution in (127a):

$$W = \frac{4\,l\,B}{3\,m^2}\left\{k\,T\,\frac{U_1}{U_0}\frac{\partial}{\partial x}\,[(k\,T)^2\,U_1] - \frac{\partial}{\partial x}\,[(k\,T)^3\,U_2]\right\} \tag{132}$$

$$= \frac{4\,l\,B}{3\,m^2}\left[(k\,T)^3\,\frac{U_1}{U_0}\frac{\partial U_1}{\partial x} + 2\,\frac{k^3\,T^2\,U_1^2}{U_0}\frac{\partial T}{\partial x} - (k\,T)^3\,\frac{\partial U_2}{\partial x} - 3\,k^3\,T^2\,U_2\,\frac{\partial T}{\partial x}\right]$$

From equations (117) and (118)

$$\frac{U_1}{U_0}\frac{\partial U_1}{\partial x} = \frac{\partial U_2}{\partial x} \tag{133}$$

Whence,

$$W = \frac{4\,l\,B\,k^3\,T^2\,U_1}{3\,m^2}\left(2\,\frac{U_1}{U_0} - 3\,\frac{U_2}{U_1}\right)\frac{\partial T}{\partial x} \qquad (134)$$

Substitutions corresponding with equation (123) for B and with (119), (120) for U_1 and U_2, give for the coefficient of thermal conductivity:

$$\kappa = -\frac{W}{\frac{\partial T}{\partial x}} = \frac{8}{9}\,\frac{\pi^3\,l\,k^2\,T}{h}\left(\frac{3\,n}{8\,\pi}\right)^{2/3} \qquad (135)$$

From equations (129) and (135), it follows that the Wiedemann-Franz ratio $\frac{\kappa}{\sigma}$, according to the Fermi statistics, has the value $\frac{\pi^2}{3}\left(\frac{k}{e}\right)^2 T$, or 7.1×10^{-11} for a temperature of 291°K. This value is in remarkably close agreement with the mean value of the ratio for the twelve common metals Al, Ag, Au, Cd, Cu, Fe, Ni, Pb, Pt, Sn, Zn; the individual experimental values however depart appreciably from this mean value.

In spite of the closely agreeing value for the Wiedemann-Franz ratio, a glance at formula (129) for the coefficient of electrical conductivity reveals the fact that it does not give the proper temperature coefficient of the conductivity,—at least if l is assumed independent of the temperature (i.e., independent of the average velocity, $\bar{v}$). Sommerfeld has shown that the same formulas (129) (135) are obtained if, throughout the calculation, l is considered as a function of the velocity. According to the wave-theory of electrons, developed by Houston and Bloch, the quantity l is a function of temperature, the atoms of the metal becoming more effective in electron-scattering the higher the temperature. Houston has shown theoretically by this method of reasoning that the conductivity of a perfect crystal varies inversely as the temperature over a considerable range of temperature.

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