Statistical Theories of Matter, Radiation and Electricity[1]

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The atomic or "kinetic" theory of gases, with its interpretations of such qualities as temperature, pressure, viscosity and conductivity, has ranked for more than half a century as a very important part of theoretical physics. A corresponding theory for radiation and for negative electricity is much to be desired, since it is known that in many ways each of these entities behaves as though it were atomic. There are, however, differences among the three, and only within the last five years have these been formulated suitably. This article is devoted to the resulting statistical theories.

THE major subjects of this article are two extensions of what formerly was called *atomic theory*—that is to say, the attempt to explain as many as possible of the properties of pieces of matter large enough to be visible and tangible and ponderable, by visualizing these as swarms of tiny particles each endowed with only a very few and simple qualities. Among the properties of gases, for example, are pressure and viscosity and entropy and temperature. Conceivably one might invest the ultimate atoms with all four. The atomic theory of gases as it stands today, however, is the outcome of a very different procedure. It is the achievement of an effort to interpret these four properties and several more as features of a hypothetical assemblage of very many corpuscles all alike, and not possessing them nor any others except position and velocity and mass (and moment of inertia, sometimes) and the liability to make elastic impacts with each other. On the whole the effort has been remarkably successful. Therefore viscosity and temperature and entropy are not attributed to single atoms, but pictures and expressions for them are derived as qualities of the assemblage. The theory which leads to these results is called *statistical;* it is based on certain assumptions which, in the form in which they were originally made, constitute the *classical statistics.* The successes of the classical statistics are a part of the evidence that matter is corpuscular. Once they were nearly the whole of the evidence, for they antedated the striking demonstrations of individual atoms which now spring to the mind whenever one is asked to state the reasons for accepting the atomic theory.

Radiation resembles a gas in some respects. Entropy and temperature and pressure, for example, are properties displayed by radiation when enclosed in a space surrounded by a wall of even temperature, just as they are by a gas in a like situation. It seems quite natural that one should try to interpret them in the same way as for a gas they are interpreted by the atomic theory: imagining the radiation

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as an assemblage of innumerable particles, a swarm of photons or corpuscles of light. Nowadays at least the idea seems quite natural; but of course, in the years when no one as yet had broken away from the tradition that light is altogether wavelike, it would doubtless have been thought a very wild one. Even after Einstein had ventured such a breach with the past, nearly a score of years elapsed before there was developed out of the theory of quanta an adequate conception of the "radiation-gas." The historical sequence in the growth of the atomic theory of matter was here inverted: there was abundant evidence for the corpuscular theory of light, in phenomena such as the Compton effect and the photoelectric effect showing the work of individual photons, before the statistical theory of these corpuscles was perfected. We now see that the trouble was, that even when one accepts the notion of corpuscles of light without reserve, and even when one knows the proper values of energy and momentum to be assigned to these corpuscles, it still is not correct to apply to them the same statistics as gives such good results when applied to the atoms of matter. Bose discovered how to remodel the statistics, in order to construct a competent atomic theory of the radiation in thermal equilibrium in an enclosure.

The other of the new extensions of atomic theory is partly a revival—the resurrection of the theory, first proposed some thirty years ago, that part at least of the negative electricity within a metal acts like a swarm of freely-flying corpuscles which collide now and again not with each other but with the atoms. It was of course the classical statistics which was always used in developing this theory. Moribund because of several incurable discordances with fact, the theory was resuscitated by Pauli and by Sommerfeld with a revision of the statistics. It was not quite the same revision as enabled Bose to set up an atomic theory of radiation, but a very similar one, invented first by Fermi and later independently by Dirac. One cannot say that the so-renovated "electron-gas theory" is a perfect explanation of all the multifarious phenomena of the flow of electricity and heat inside of metals and outward through the boundaries of metals. Its initial successes, however, are so auspicious as to suggest that the hope of further progress lies not in renouncing it (as seemed to be almost inevitable before the alterations) but in amending it in its details.

Is the atomic theory of material gases to remain untouched by these novel ideas? Apparently all three forms of statistics, the classical and the two recent types, lead to very nearly the same conclusions when applied to material gases. Only at remarkably low temperatures and remarkably high densities do their predictions diverge; and under these conditions the experimental data are not easy to interpret for that purpose. Suppose, however, that eventually the data are proved to decide for one of the new forms of statistics against the old: what then? Probably we shall merely remove one of the theoretical foundation-stones of the kinetic theory of gases and insert another to take its place, meanwhile leaving practically intact the great superstructure of formulæ and equations whereby the kinetic theory makes contact with experience. Happily this is an easier process in theoretical physics than in architecture.

Custom has lately changed the meaning of the term *atomic theory*, making it almost synonymous with *theory of the structure of the atom;* but the province which this latter has taken for its own is one to which its forerunner disclaimed all right of entry. It was never supposed that all of the properties of a gas can be interpreted as statistical features of a swarm of corpuscles. The earlier atomic theory conceded some of them to the individual atoms, thus in effect renouncing the ambition to explain them; and among these were the spectra. Where the statistical theory left off, the builders of atom models took up the work. Bohr, for example, designed a model for the individual hydrogen atom, competent—at least to a great extent—to explain the Balmer series and the rest of the line-spectrum of "atomic hydrogen." This model he constructed, following Rutherford, out of a pair of corpuscles. What he and his successors thus developed was in a way an *atomic theory of the atom*—a degree deeper, or further, or higher perhaps, then the atomic theory of matter which had provided him with the notion and the scale of the atom to begin with.

What then distinguishes this new "atomic theory of the atom" from its ancestor? Well, the major differences in method and in aim are traceable to the fact, that in the later theory the number of elementary particles which constitute the system is quite manageably small, while in the earlier, it is inconceivably tremendous.

Bohr constructed his model for the hydrogen atom with only a pair of corpuscles, and those for all the other atoms out of not more than a few dozen each. Now with a model consisting only of two particles, one can specify positions and velocities for these with the utmost of precision, and go merrily ahead predicting and describing orbits with as much exactness as one cares to lavish. Even with dozens of electrons and a nucleus one can attain at least a specious accuracy of detail; remember the portraits of the electron-orbits of massive atoms which six or seven years ago were so profuse. Perhaps it is not wise to make such definite assertions; but it is feasible. Not so, however, with the subjects of the older theory.

The model proposed for a cubic centimetre of gas under the ordinary conditions of temperature and pressure consists of something like 10^{20} particles. Merely the mention of so extravagant a figure is sufficient to persuade that it is vain to dream of making any progress by postulating a definite position and a definite velocity for each of these. The life of the human race would not be long enough to write down even the postulates, to say nothing of the inferences.

This seems a fearful handicap; but it is not so at all. Adopting the statistical method, one does not even begin upon the hopeless task of fixing place and motion for every particle. We content ourselves with writing down a function, which states how many among the multitude of particles we assume to be situated in each small (but not too small) element of volume; and how many we assume to have momenta which lie in each small (but not too small) range of momentum. These are specifications much more modest and vague; but they are ample. For the things which we wish to interpret—entropy and temperature, viscosity and conduction and diffusion—the atomic picture need not be made one whit more definite.

In saying this I am understating the case. If the atomic picture could be made more definite, say by stating the locations and the velocities of all the atoms with absolute precision, the meanings which we shall presently attach to entropy and temperature would be dissolved. Our theory of these entities depends upon the vagueness of the picture. Seemingly they appeal to us as physical realities because our senses and our instruments are too obtuse to perceive the atoms. Our minds must feign a somewhat similar obtuseness, pretending not to fix the particles of the imagined swarm too sharply; therefore it does not matter that they are so numerous that the pretence becomes sincere. Exact knowledge of the individual atoms is unattainable; but it is useless, is not desirable even. One remembers Æsop's tale of the fox and the inaccessible grapes; in this case it is probable that the grapes really *are* sour.

For that matter, perhaps they do not even exist. One of the most striking of the very recent ideas in theoretical physics is the thought, that even for atom-models with but a few particles, even in thinking of an isolated particle, it may be altogether pointless to assign exact positions and velocities. In dealing with a swarm of particles by the statistical way, we do in effect fix the position of each corpuscle, but with a certain latitude; we fix the velocity of each, but again with a certain latitude. Perhaps this latitude, this indefiniteness, is something inherent in nature. Insisting as I am upon the contrast between the theory of the structure of the atom and the statistical theory of matter and radiation, I may in effect be insisting on the contrast between a faulty way of visualizing some phenomena, and a correct way of visualizing all.

A function of the sort which I just mentioned, a so-called *distribution-function*, is the goal of every statistical theory. I have said that it states how many among the multitude of particles we *assume* to be located in each small element of space and to have momentum comprised in each small range of values of momentum. So it does; but the purpose of a statistical theory is, to derive it from assumptions still more fundamental, in preference to assuming it outright. Of course one might say instead, that the reason for deriving a distribution-function is to put the fundamental assumptions to their test. Whichever viewpoint one prefers, it is the distribution-function which is tested by experiment: indirectly, in that it supplies numerical values for such things as conductivity, viscosity, specific heat; and directly, for there are now immediate ways of observing it in certain cases.

A distribution-function commonly appears in an equation of this form:

$$dN = f(x, y, z, p_x, p_y, p_z) \cdot dxdydzdp_xdp_ydp_z. \tag{1}$$

Such an equation will as a rule refer to some particular assemblage of particles, say N altogether, occupying some definite region of space: a gas in a tube, radiation in a cavity, electrons in a wire. It is to be read as follows: "dN, equal to $f \cdot dxdydzdp_xdp_ydp_z$, stands for the number of particles having coordinates in dx at x, in dy at y, in dz at z, and components of momentum in dp_x at p_x, in dp_y at p_y, in dp_z at p_z." The phrasing "in dx at x" is a succinct alternative for "between x and $x + dx$."

The function f is the distribution-function in the variables in question—here the *coordinates* of the particles referred to some Cartesian frame in the ordinary or "coordinate" space, and the components of momentum resolved along the axes of that frame, the *momenta*. Heretofore it has been customary to use the components of velocity rather than the momenta, but these are much to be preferred: partly because it is they which figure in the canonical equations, but chiefly because we shall find when we pass over to the study of assemblages of photons that the momenta play the same role in these as they do in assemblages of atoms, while the speeds of all photons are the same. There is a well-known formula for translating a distribution-function from one set of variables to another set dependent on the first, which we shall use in special cases.[2] It is also well known that to obtain the distribution-function in *some* of the independent variables from the distribution-function of *all* of them, it is necessary to integrate the latter over the entire range of all the *other* variables: in such a case as is symbolized by equation (1), the distribution in p_z would be obtained by integrating f with respect to the first five variables over the entire range of each.

The product $dxdydz$ is an element of volume in ordinary or *coordinate-space;* the product $dp_xdp_ydp_z$ is an element of volume in *momentum-space*, in which each particle is represented by a point having for its coordinates in a Cartesian frame the values of its momenta; the product $dxdydzdp_xdp_ydp_z$ is an element of volume in *phase-space*. The function f describes the distribution of the assemblage in this phase-space of six dimensions. In some cases—for instance, that of electrons in a metal not at an even temperature, and that of oscillators—we shall have to think continually of this six-dimensional space. In others—whenever we deal with photons, and whenever we consider atoms or electrons in a region where neither temperature nor potential varies from place to place—we shall be able to assume that the distribution in the coordinate-space is uniform (that f is independent of x, y, z) and to dismiss it from mind, and to derive the distribution in the three-dimensional momentum-space quite separately as if there were no other. Even in these simplest cases it would no doubt be more consistent to operate always in the phase-space. Unhappily the human mind is so constructed, that no matter how much it may ratiocinate about space of six dimensions or six trillion, it always visualizes in space of three.

In an equation such as (1), the differential element or the product of such elements which terminates the right-hand member must be neither too large nor too small. If it is so large that f varies considerably from one point in it to another, then its multiplier, which is by definition the *mean value* of f in the said element, must be computed by the methods of integral calculus. If on the other hand it is so small that it contains only a few of the corpuscles, then the product of f into its size may be many times as great or many times as small as the number which it does contain. This is easily perceived by proceeding to the absurd limit of dividing the space into say ten times as many elements as there are corpuscles, so that in at least

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[2] Let $u_1, u_2, \cdots$ represent the variables of the first set, $v_1, v_2, \cdots$ those of the second; let $f(u_1, u_2, \cdots)$ and $F(v_1, v_2, \cdots)$ stand for the distribution-functions in the two sets; then

$$F(v_1, v_2, \cdots) = f(v_1, v_2, \cdots, \frac{\partial(u_1, u_2, \cdots)}{\partial(v_1, v_2, \cdots)} \cdot$$

nine-tenths of the elements the number of participles is zero while f is greater than zero, and in the others the number is generally much greater than f times the size of the element. To subdivide the space so finely would be to make the atomic picture too definite, and ruin it for the purposes for which we now require it.

It is not too early in this paper for me to say emphatically that the differential elements which figure in equations such as (1) *must not be identified* with the elementary compartments of the phase-space, which we shall presently encounter, and which are so important in the new statistics and in the old alike. It takes a great many of these latter to make up an element large enough to be employed in an equation like (1). Otherwise expressed: the subdivision of the phase-space into the elementary cells or compartments of the forthcoming theory is much too fine to be used in connection with the distribution-function. Much confusion may arise from failing to realize this.[3]

In speaking of the distribution-function, I have been tacitly assuming that there is such a thing as a stable, self-sustaining, changeless distribution of the atoms of a gas, the photons in a cavity, the electrons in a wire. This assumption must now be examined. It is scarcely self-evident; one might guess at first that the more numerous the particles, the more abruptly would the distribution vary from one moment to the next, and that an assemblage of 10^{20} particles would be in such unceasing turmoil that it would be senseless to imagine one single distribution for it.

Experience however shows the reverse. The gas in a tube remains uniformly dense and stationary, it does not surge forever to and fro nor huddle in a corner nor become spontaneously hot at one end and cold at the other. In the radiation in a cavity with heated walls the intensity comprised within any portion of the spectral range remains unchanged so long as the temperature of the walls is constant. The distribution-in-velocity of the electrons streaming from a heated filament does not appear to change. Moreover, when by artifice the gas in a tube is forced to assume uneven density, non-uniform temperature, or any sort of flow or turbulence, it settles down very quickly into a stagnant uniformity as soon as it is left to itself.

Now we know that while a gas is passing from an unstable state—a state of non-uniform temperature, for instance—to its stable and permanent condition, a property which we call its *entropy* and denote

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[3] I am thinking particularly of the fact that in most expositions of the classical statistics one is adjured that there must be many particles in each compartment, and then in taking up the Fermi statistics one is told that there must be not more than one in each compartment; yet the two lead to formulæ which in the limiting case are the same.

by S is increasing; in certain simple cases we can evaluate this rate of change of entropy. We know that when a gas is in its stable condition, its entropy is at a maximum; we know how to compute the entropy (except perhaps for an additive constant) of a given quantity of a gas in this condition, as a function of its temperature and others of its measurable properties. And when we have evaluated both the entropy S and the energy E of a gas under any specific conditions, we know that its absolute temperature is determined by the following equation,

$$dS/dE = 1/T, \tag{2}$$

which is the definition of absolute temperature.

If we had obtained by some independent way an adequate atomic picture of entropy, so that whenever a distribution-function was suggested we could compute the value of S: then necessarily the stable distribution would be the one for which S has the greatest value compatible with the given number of particles and the given amount of energy. We do not have an independent way. But if instead we adopt some *tentative* atomic picture of entropy, some function S of which we can compute the value for any given distribution: then the test of our picture will be, whether the distribution for which this tentative S has its greatest value is verified by experiment to be the stable one. It will be found that this distribution "of maximum S" involves the derivative dS/dE, and therefore the absolute temperature; so the temperature enters into the postulated distribution-function in the course of its derivation, not by separate assumption or by an afterthought.

This method is the very notable one invented by Boltzmann, and continued by Planck. One choice of the function S which is to be identified with entropy leads to the classical or Maxwell-Boltzmann distribution-law; another leads either to the Bose or to the Fermi distribution, the difference between these two entering in at another point.

Each of these suggested functions is logarithmic; it is proportional to the logarithm of a function which is called *probability*. In theoretical physics it is a fairly general rule, that when a theorist introduces the word *probability* he is abandoning all hope of explaining by cause-and-effect the phenomena of which he is discoursing. This is the disadvantage of Boltzmann's method. The "distribution of maximum S" is baptized "the most probable distribution"; there is even a numerical estimate of its "probability," and in general it turns out to have so much greater a probability than all the others put together that one accepts without demur the conclusions that in practice it will be stable. But there is no proof that the "most probable" distribution is always or even usually followed by another exactly like it, nor that an "improbable" distribution is always or even usually followed by another of greater probability; there is no study of the way in which one distribution is transformed into another, there are no assumptions about the collisions or encounters which presumably offer to the particles their means of interchanging speed and energy, and to the assemblage its means of approaching the stable distribution. There are other statistical methods in which account is taken of these things, and we shall have a glimpse of one of them in the last section of this paper; but the notion of causality is absent from the method which will be followed in deriving the distribution-laws of Maxwell and Boltzmann, of Bose, and of Fermi and Dirac.

These three distribution-laws will be applied to freely-flying particles in regions which are either field-free, or else pervaded by a field (electrostatic or gravitational) derivable from a potential. It may surprise the reader to hear so little about oscillators, considering that the statistics which Planck applied to these objects was the first of all the modifications of the classical statistics, was the source of the entire quantum-theory, and therefore the most important advance of the physics of the last quarter-century. The history of this period is very curious; but I cannot mention more than a couple of the salient points.

The Planckian oscillators served two purposes: they enabled Planck to derive the law of distribution of radiant energy at uniform temperature in a cavity, by supposing the radiation to be entirely wavelike and to be in equilibrium with myriads of oscillators in the walls of the cavity; and they enabled various savants to develop, step by step, a progressively improving theory of the specific heat of solids. The Bose statistics made them quite superfluous for the first purpose: by applying this statistics to the radiation supposed to consist of corpuscles, we can derive the same law of distribution without invoking the oscillators at all. As for the second: as early as 1912 (which seems remarkable, now) Debye had replaced the concept of a solid as a latticework of vibrating atoms by the concept of a solid as a system of stationary waves agitating a continuum. I do not mean to imply, of course, that the existence of the atoms was denied; I mean no more than to say, that in these statistical reasonings the individual vibrating atom was replaced by an individual pattern of stationary waves. Today we are becoming familiar with the idea that in certain reasonings, a freely-flying electron or quantum or even an atom in a region bounded by walls may be replaced by a pattern of stationary waves filling the whole of this region. Thus it seems that the free particle, the oscillator, the stationary wave-pattern, are in close affinity with one another; they may simply represent different ways of looking at the same thing. Though on almost every page of this article I shall write in the language of the strictest corpuscular theory, it is probable that every one of the results could be translated into the language of oscillators or the language of waves.

There are still assumptions to be made about the individual particles. They are to have position, momentum and energy. Momentum may be separated into mass and velocity; often it is better left as an elementary concept. It will turn out that one of the essential differences between photons on the one hand, electrons and atoms on the other—that is to say, between the particles out of which we shall try to build a picture of radiation, and those of which we shall build models of gases and of electricity in metals—lies in the relation between momentum and energy.

Experience with matter in bulk leads to the well-known equations connecting kinetic energy K and momentum p with mass m and speed v:

$$K = \tfrac{1}{2}mv^2, \qquad p = mv \tag{3}$$

and these are supposed to hold for the ultimate particles of matter and of electricity.

During the years in which the corpuscular theory of light was struggling into existence—for, it will be remembered, light was still considered to be entirely wavelike even after Planck had founded the quantum-theory by his statistics of oscillators—Einstein proposed at two different times (1905 and 1917) the following formulæ for the energy and the momentum of photons in terms of their wavelength:

$$E = hc/\lambda, \qquad p = h/\lambda. \tag{4}$$

Historically it is interesting that he proposed the latter formula because of certain statistical studies which he had made of the equilibrium between photons and atoms. The verification of the latter by the Compton effect, of the former by the photoelectric effect and many other phenomena, is too familiar to require comment.

Now from equations (3) we deduce, for particles of matter and of electricity:

$$E = \frac{1}{2m}p^2 = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \tag{5}$$

and from equations (4) we deduce, for particles of light:

$$E = pc. \tag{6}$$

The difference between these two relations is responsible for some of the contrasts between radiation-gas on the one hand, electron-gas and material gases on the other; but by no means for the major part. The major difference lies in the statistical theory, as we shall now find out.

THE CLASSICAL STATISTICS

We are going to represent three kinds of objects—ordinary or material gases, radiation in enclosures, negative electricity in metals—as assemblages of particles possessing location and momentum. We may visualize such an assemblage first as a swarm of points in ordinary space, with a coordinate-frame along the axes of which the coordinates x, y, z of the particles are measured; then as a swarm of points in momentum-space with a frame along the axes of which the momenta p_x, p_y, p_z are measured.

I will first illustrate the method of classical statistics by using it to ascertain the most likely distribution of particles in ordinary space, a case where seemingly the result may be foreseen. For it seems a truth of intuition that inside a box of ordinary space, with nothing (*e.g.* no variations of potential) to distinguish one region from another, the particles must tend to distribute themselves uniformly. This is a conclusion to which the statistical method *must* lead. The uniform distribution *must* be the most probable. How then should we define the "probability" of a distribution so that it shall be greatest for the uniform one?

But in the first place, what *is* a uniform distribution? We must divide the space—mentally, of course—into conpartments of equal volume. The distribution will then be called uniform, if the numbers of particles in the various compartments are about the same. But this clearly requires that these subdivisions be of a certain size. Their linear dimensions cannot for example be smaller than the average distance between particles, as then a "uniform distribution" would be impossible. To partition the space too finely would be like studying a painting with a microscope. The quality which we wish to define evades too sharp a scrutiny. The compartments should contain large numbers of particles, both for the stated reason and for the convenience of a certain mathematical approximation which is made.

Denote then by N the total number of particles, by m the number of compartments into which the volume V is divided, by N_i the number of particles in the ith compartment. A distribution is described by stating all the numbers $N_1, N_2 \cdots, N_i, \cdots N_m$.

The basis of the classical statistics is the fact that if the particles have identities—if each of them is labelled by a distinctive letter, for instance—there are different ways of arranging them in the same distribution. One starts with any arrangement compatible with the prescribed "populations" $N_1, N_2, \cdots N_m$, and obtains all the other arrangements by interchanging particles *ad libitum* among the compartments, respecting only the condition that each of these shall always have as many as it had at first. The total number of distinct arrangements, the number of *permutations of the combination* $N_1, N_2, \cdots N_m$, is by a well-known theorem:[4]

$$W = \frac{N!}{N_1!N_2!\cdots N_m!} \cdot \tag{7}$$

This number has its minimum value of unity for a distribution in which all the particles are crowded into one compartment, which would be the most non-uniform conceivable; and its maximum value for the uniform distribution, as I now proceed to show.[5]

Let us use the logarithm of W instead of W itself. If W has a maximum for any distribution so also will its logarithm, which is easier to handle, and will presently be chosen as the representation of entropy. We have:

$$\log W = \log N! - \sum \log N_i!. \tag{8}$$

Now we introduce Stirling's approximation for the factorial of a large number—by far the greatest and the most frequently invoked

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[4] Imagine yourself stationed beside a set of m baskets and an urn filled with N lettered but otherwise indistinguishable balls, which are to be lifted out at random and dropped into the baskets under the following rules of the game: the first N_1 which come to your hand are to be dropped into basket 1, the next N_2 to come to your hand are to go into basket 2, and so on to the end. Having acted accordingly, you note down the assortments of balls in the various baskets, and repeat the process *ad infinitum*. Now there are $N!$ different orders in which the balls may come out of the urn. When the inspection of the baskets after two drawings reveals different results, the orders must certainly have been different. But two different orders need not reveal two different results to the inspection. Take any order, to start with; then there are $(Q - 1) = (N_1!N_2! \cdots N_m! - 1)$ others which yield the same result. For there are $N_1!$ orders in which the earliest N_1 balls emerge might come out, without any of them losing its place among the first N_1; there are $N_2!$ orders in which the next N_2 might come, without any losing its place in the second basket; and so forth. Each of the $N!$ orders then is but one among Q altogether which lead to the same result; so that there are only $N!/Q$ different results.

[5] What will actually be shown is that for the uniform distribution the function W is stationary; that it is maximum (not minimum) seems fairly obvious from the physics of the case, and can be proved.

of the mathematical aids in statistical theory. It is:

$$\begin{aligned} x! &= (2\pi x)^{1/2}(x/e)^x, \\ \log x! &= x \log x - x + \tfrac{1}{2}\log(2\pi x). \end{aligned} \tag{9}$$

The first two terms of this latter expression form an approximation singularly good even when x is no greater than ten or thereabouts. Using it we have:

$$\log W = \text{const.} - \sum N_i \log N_i. \tag{10}$$

Denote by W^0 the value of W for some particular distribution $N_1{}^0$, $N_2{}^0$, $\cdots N_m{}^0$ and by $W = W^0 + \delta W$ its value for some other only slightly different distribution $N_1{}^0 + \delta N_1$, $N_2{}^0 + \delta N_2$, $\cdots N_m{}^0 + \delta N_m$. The difference between the values of log W for these two distributions is to first order of approximation:

$$\delta \log W = \delta W / W = -\sum_i (1 + \log N_i{}^0)\delta N_i. \tag{11}$$

If W^0 is a maximum for the distribution $N_1{}^0 \cdots N_m{}^0$, then the difference between log W^0 and the value of log W for any other slightly different or "slightly varied" distribution must vanish to first approximation. The quantity on the right of (11), the "first variation" of log W, must be zero for any permitted set of values of $\delta N_1, \cdots \delta N_m$; meaning by "permitted" any set of integer values adding up to zero, for we consider an assemblage of an invariable number of particles.

Now one sees immediately that the right-hand side of (11) does vanish, if all the populations $N_i{}^0$ have the same value, say α; for then

$$\log W = -\sum_i (1 + \log \alpha)\delta N_i = \text{const.} \sum_i \delta N_i \tag{12}$$

and the permitted variations are precisely those, for which the summation $\sum N_i$ is zero.

We do therefore reach the result which was desired. Failing it, this mode of "counting the ways in which a distribution may be realized" would have been unprofitable. As it is, the quantities W and log W are greatest for the uniform distribution which seems intuitively the most probable and is the rule for gases, and least for the utterly non-uniform one which seems the least probable. Tentatively the former is adopted as measure of the "probability" of a distribution.

I point out in passing that while the foregoing result is mathematically valid for any value of the constant α, the total number of particles prescribed for the assemblage determines the value of α which is physically permissible: viz. N/m.

We proceed to apply this method to the swarm of points in momentum-space representing the assemblage.

Like the coordinate-space, the momentum-space is to be divided into equal compartments large enough to contain each a multitude of particles. We are to define a distribution by specifying how many particles are in each compartment, and calculate as before the number W which is to measure the "probability" of the distribution. The values for W, for $\log W$ and for the variation of $\log W$ are obtained just as before. There is however an important novelty. Since the energy of a particle depends on its position in momentum-space, different distributions usually entail different values for the total energy of the assemblage. If we compute the variation of $\log W$ due to a slight change in distribution, we shall usually be computing a variation in $\log W$ correlated with a certain variation of the total energy U of the assemblage.

We now take the very great step of *identifying the quantity log W with entropy.*

More precisely, we assume that the entropy S is proportional to the logarithm of W:

$$S = k \log W, \tag{13}$$

introducing a constant factor k, and relying on subsequent experiments to teach us its numerical value.

Now when a gas being initially in thermal equilibrium at temperature T receives an infinitesimal amount of energy dE, and regains thermal equilibrium with its augmented energy, its entropy ascends by the amount of dS given by the equation:

$$dS/dE = 1/T. \tag{14}$$

If then the foregoing model of the gas and the foregoing picture of entropy are justified, the variation of $\log W$ in passing from the most probable distribution consonant with a total energy E to the most probable distribution consonant with a total energy $E + dE$ (the total number of particles remaining the same) must be equal to $(1/kT)dE$.

If we start from the most probable distribution for energy E and make *any* slight change in it involving an energy-change dE, the new distribution will presumably differ but little from the most probable distribution for $E + dE$. We therefore say: the most probable distribution for energy E is the one of which the first variation is dE/kT. This expression vanishes, if we are comparing distributions for which E is the same; which is as it should be.

It is now easily shown that such a distribution is the following

$$N_i = \alpha \exp\,(-\,\epsilon_i/kT), \tag{15}$$

in which α stands for any constant and ϵ_i for the average energy of particles in the ith compartment, which is related to the average momenta of these particles by the equation

$$\epsilon = \frac{1}{2m}\,(p_x^2 + p_y^2 + p_z^2)' \tag{16}$$

for we have only to write down the expression for δS as furnished by equation (11), and introduce into it the value of log N_i as supplied by equation (15):

$$\begin{aligned} \delta S = &-\,k\textstyle\sum(1 + \log N_i)\delta N_i \\ &= -\,k(1 + \log \alpha)\textstyle\sum\delta N_i + \textstyle\sum\epsilon_i\delta N_i/T = \delta E/T, \end{aligned} \tag{17}$$

the result which was desired.

The value to be chosen for the constant α will be determined as before by the total number of particles. Denote this number by N, and conceive the compartments as tiny cubes of volume H, so that there are $1/H$ of them per unit volume of the momentum-space. The density ρ of the particles in momentum-space, which is no other than the *distribution-function in the momenta*, is given anywhere by the value of N_i/H computed for the value of energy there prevailing:

$$\begin{aligned} \rho &= N_i/H = \frac{\alpha}{H}\exp\,(-\,\epsilon/kT) \\ &= \frac{\alpha}{H}e^{-p_x^2/2mkT}e^{-p_y^2/2mkT}e^{-p_z^2/2mkT} \end{aligned} \tag{18}$$

and it is the integral of this expression over the whole of momentum-space which is equal to N:

$$N = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\rho\, dp_x dp_y dp_z. \tag{19}$$

The integration is easily affected; the triple integral is the product of three identical single integrals, and we have:

$$N = \frac{\alpha}{H}\left[\,(2mkT)^{1/2}\int_0^{\infty} e^{-w^2}dw\,\right]^3, \tag{20}$$

w being a symbol for each of the three momenta in turn; so that

$$\alpha = \frac{NH}{(2\pi mkT)^{3/2}}\cdot \tag{21}$$

The expression for the number of particles in any compartment thus becomes:

$$N_i = \frac{NH}{(2\pi mkT)^{3/2}} \exp\,(-\,\epsilon_i/kT), \qquad (22)$$

involving the four constants m, N, k and H. The first three are determinable by experiment, the third is the universal constant known in Boltzmann's honor by his name, though he himself never evaluated it. The fourth, the volume H assigned to the compartments, drops out of the distribution-functions—out of the function ρ, out of the distribution-in-energy soon to be deduced, out of the fundamental distribution-function f in the coordinates and momenta defined by equation (1), and which I now set down in place of ρ:

$$f = \frac{N}{V(2\pi mkT)^{3/2}} \exp\left(-\,\frac{p_x^2 + p_y^2 + p_z^2}{2mkT}\right), \qquad (23)$$

V standing for the volume in ordinary space of the enclosure which contains the assemblage. This evasion of H is very deceptive; for it suggests not merely that the exact volume of the compartments is of no importance, but that the compartments themselves were invented only as a momentary stepping-stone to the distribution-functions, and should be allowed to shrink to zero like the infinitesimals of the calculus. This however is precisely what is not allowed. It is of the essence of the argument that there are compartments of finite size. As will presently transpire, I suspect that the division of momentum-space into compartments should be regarded as a quantum postulate, even in this case of the derivation of the Maxwell-Boltzmann law which seems to be at the opposite extreme from all the notions of quantum-theory.

The next step is the derivation of the *distribution-in-energy*. In preface I point out that the distribution which we are considering is, in respect to the directions of motion of the particles in ordinary space, *isotropic*. Mathematically, this occurs because p_x, p_y and p_z enter symmetrically into all the distribution functions; physically it occurs because we have made no assumption leading to a preference of any direction over any other. Later on we may establish a preferred direction by introducing a field of force, and then the impending steps may have to be reconsidered. Until then the distribution which we shall study will be described completely by saying that they are isotropic and giving the distribution-function-in-energy. This may be obtained from the distribution-function-in-the-momenta by transforming to a polar coordinate frame in the momentum-space.[6]

I follow practically the same route.

Divide up the momentum-space into spherical "shells" by means of a sequence of spheres all centered at the origin. Each sphere corresponds to a value of ϵ, each shell to a range $d\epsilon$ of values of ϵ. Take one of the latter at random; call it shell s, denote by ϵ_s and by ϵ_{s+1} or $\epsilon_s + d\epsilon$ the energy-values at its boundary spheres, by r_s and $r_s + dr$ the radii of these, by dV the volume of the shell. Then:

$$r_s = (2m\epsilon_s)^{1/2}, \qquad dr = \left(\frac{m}{2\epsilon_s}\right)^{1/2} d\epsilon,$$

$$dV = 4\pi r_s^2 dr = \frac{2}{(\pi)^{1/2}}(2\pi m)^{3/2}(\epsilon_s)^{1/2} d\epsilon. \tag{24}$$

Suppose to begin with that each shell is large enough to contain very many compartments. The number Q_s of compartments in shell s will then be:

$$Q_s = dV/H = \frac{2}{H(\pi)^{1/2}}(2\pi m)^{3/2}\epsilon_s^{1/2} d\epsilon \tag{25}$$

and the average number of particles per compartment in shell s, call it N_s, will be:

$$N_s = \alpha \exp\left(-\epsilon_s/kT\right) \tag{26}$$

and the total number M_s of particles in the shell will be:

$$M_s = Q_s N_s = \frac{2N\pi}{(\pi kT)^{3/2}} \epsilon_s^{1/2} e^{-\epsilon_s/kT} d\epsilon = F(\epsilon_s) d\epsilon. \tag{27}$$

This is the number of particles having energy-values in $d\epsilon$ at ϵ_s. Hence the distribution-function-in-energy F is the factor multiplying $d\epsilon$ (it would be well to discard the subscript s in writing it). I have copied the value of α from (21), but it could have been derived by integrating F from $\epsilon = 0$ to $\epsilon = \infty$ and equating the integral to N.

The separation of M_s or $F(\epsilon)d\epsilon$ into two factors—Q_s the number of compartments in the shell s, N_s the average number of particles per compartment—is highly advantageous in searching for the distinctions

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[6] Denote by p the quantity $(p_x^2 + p_y^2 + p_z^2)^{1/2}$ which is the magnitude of the momentum; and by θ and ϕ the angles which with p constitute a spherical coordinate system. We have

$$\rho\, dp_x dp_y dp_z = \rho p^2 \sin\theta d\theta d\phi dp = \frac{\alpha}{H} e^{-p^2/2mkT} p^2 \sin\theta d\theta d\phi dp$$

and the distribution-in-momentum is obtained by integrating over all values of θ and ϕ, the distribution-in-energy from it by means of the relation (5).

between the various proposed statistical laws. We shall see that in passing from one to another sometimes one of the factors is changed, sometimes the other, sometimes both.

In particular, we may pass from the Maxwell-Boltzmann law to a distribution like that which Planck derived for oscillators, simply by changing the factor Q_s. We have been dividing the momentum-space into compartments of equal volume, so that the number comprised in a shell s between spheres ϵ_s and $\epsilon_s + d\epsilon_s$ is proportional to $\epsilon_s^{1/2}d\epsilon_s$. Let us instead divide it into compartments of which the volumes increase steadily from the origin outward, at such a rate that the number in a shell s is proportional to $d\epsilon_s$ without the factor $\epsilon_s^{1/2}$.

This is, of course, not the way in which Planck's postulate is habitually stated, though it is substantially the way in which Planck stated it himself. Usually it is said, that Planck restricted the energy of the particles of the assemblage to a set of "permitted values" spaced at equal intervals: say the values a, $a + b$, $a + 2b$, $a + 3b$, $\cdots$ where a and b stand for constants. Each of these permitted values corresponds to a sphere in the momentum-space. In the shell s there are approximately $d\epsilon_s/b$ of these "permitted spheres"; the approximation being closer, the larger ϵ_s and $d\epsilon_s$ are in comparison to b. Now whether we conceive that the $d\epsilon_s/b$ sets of particles in the shell s are located on the surfaces of as many permitted spheres, or alternatively that they are scattered through as many compartments, is for the statistical results of no importance. There may be other reasons for preferring one picture to the other; but the predictions of the statistical theory are the same, whichever is adopted. I will therefore alternate between the two pictures, retaining for the moment that of a subdivision of the momentum-space into compartments; but now it will be expedient to think of these as thin spherical films, centered at the origin and increasing in volume from the innermost outward at the specified rate.

If the shell s is large enough to contain many of these compartments or permitted spheres, we may use the first approximation for the number which it contains:

$$Q_s = d\epsilon/b, \tag{28}$$

and putting the expression (26) for the number of particles per compartment, we get:

$$M_s = Q_sN_s = \frac{\alpha}{b}\exp\,(-\,\epsilon_s/kT)d\epsilon_s = F(\epsilon_s)d\epsilon_s \tag{29}$$

for the number of particles having energy-values between ϵ_s and

$\epsilon_s + d\epsilon_s$. The value of the constant is fixed as heretofore by the condition that the integral of F over the entire range of energy from 0 to ∞ shall be equal to N:

$$\int_0^\infty F(\epsilon)d\epsilon = \frac{\alpha kT}{b}\int_0^\infty e^{-w}dw = N, \tag{30}$$

so that we arrive at the following distribution-in-energy function:

$$F(\epsilon) = \frac{N}{kT}\exp\left(-\,\epsilon/kT\right). \tag{31}$$

This function certainly does not display any feature which suggests the achievements of Planck! It looks as smooth and continuous as the Maxwell-Boltzmann function itself, and the constant b, the step or interval between the successive permitted energy-values or the boundaries of successive compartments, is nowhere to be seen. The constant b however has slipped out for the same reason as the constant H from the function (23), and the apparent continuity is due in both cases to the same cause. In preparing and effecting the integration (30) in order to obtain a value for the constant α, we assumed that the various permitted energy-values within the range $d\epsilon_s$ are all sufficiently nearly equal to be identified with the single value ϵ_s. That is to say, we smoothed over the discontinuities which had previously been brought in by the assumption of separate compartments. No wonder that there is not a sign of them in the function (31), even as there is not a sign of them in the Maxwell-Boltzmann law!

We might however avoid this smoothing-over, if we could attain the value of α by an actual summation over the various compartments instead of by integration. Now with Planck's postulate this is mathematically feasible and indeed easy. For the number of particles in the ith compartment being

$$N_i = \alpha\exp\left(-\,\epsilon_i/kT\right) \tag{32}$$

the total number of particles is computed thus:

$$\begin{aligned} N = \sum N_i &= \alpha e^{-a/kT}\sum_{i=0}^{\infty} e^{-ib/kT} \\ &= \frac{\alpha e^{-a/kT}}{1 - e^{-b/kT}} \end{aligned} \tag{33}$$

by virtue of the very convenient consequence of the binomial theorem that $(1 + x + x^2 + \cdots) = (1 - x)^{-1}$; so that for α we obtain the *exact* value:

$$\alpha = Ne^{(a-b)/kT}(e^{b/kT} - 1) \tag{34}$$

and for the populations of the various compartments, the formula:

$$N_i = Ne^{-b/kT}e^{-ib/kT}(e^{b/kT} - 1). \tag{35}$$

Here the discontinuity implied in the classical picture of a momentum-space divided into compartments is admitted and accepted, as it never was in the process of deriving the Maxwell-Boltzmann law. Planck did not put discontinuity into the classical statistics; it was there already; he refrained from disregarding it. Instead of confining his studies to the circumstances in which it can safely be ignored, he extended them to ranges where it had to be taken account of, and he took account of it.

As I intimated, the distribution (35) was proposed by Planck not for freely-moving particles, but for oscillators. The "Planckian oscillator" may be visualized as a particle which executes simple-harmonic vibrations back and forth in a straight line across a position of equilibrium, to which it is attracted by a force proportional to its displacement. It is like a free particle, in that its state at any moment is described by giving the values of its position q and momentum p, q being measured from its point of equilibrium; but it is unlike a free particle in that its energy depends not on p alone but on both p and q, being a function of the form $(Ap^2 + Bq^2)$. Therefore we must envisage not the momentum-space alone but the phase-space of the variable p and q. In principle it would have been better, had we envisaged the phase-space all along; but since for an assemblage of free particles that space has six dimensions, it was impractical to visualize more than the momentum-space, and since the energy depended only on the momenta that compromise was not detrimental except for one feature which I can later introduce. Here the compromise would be ruinous, but it is unnecessary since the phase-space has only two dimensions.

Visualize then this two-dimensional phase-space as a plane with p and q axes at right angles to each other. Suppose all the oscillators to have the same mass and the same natural frequency, which is to say, the same values of the constants A and B in the above-mentioned formula for their energy; but let them differ in amplitude. The point representing any oscillator in the phase-space runs round and round in an elliptical orbit centered at the origin. Different amplitudes correspond to different ellipses. The energy of an oscillator depends on its amplitude; therefore different energy-values correspond to different ellipses, and reversely. If we divide the phase-space into compartments by a succession of ellipses centered at the origin, each of these compartments corresponds to a specific range of energy-values. If the dividing ellipses are so spaced that these compartments are of *equal* area (equal volume of the phase-space), they correspond to *equal* ranges of energy-values—an important difference between this case and the one which was previously treated.

If the dividing ellipses are spaced to form equal compartments, they themselves correspond to energy-values forming a linear sequence: call these a, $a + b$, $a + 2b$, $\cdots a + ib \cdots$ as before. Whether we call these the "permitted" energy-values and allow the oscillators only the choice among them, or whether we sprinkle the oscillators uniformly through the compartments, makes only a secondary difference. In this case, in fact, we can easily see exactly what difference it makes. If the oscillators are sprinkled uniformly in each compartment, then by applying the classical statistics we get just the same distribution (35) as when we assume them restricted to the energy-values $(a + ib)$. But when we undertake to evaluate the average energy of all the oscillators, then in the one case we must put down the mean energy of those in the ith compartment as the arithmetic mean of the values $a + ib$ and $a + (i + 1)b$, while in the other case we must put down the energy of those at the ith permitted ellipse as $a + ib$. Hence to change over from the picture of permitted energy-values to the picture of compartments is the same thing as to replace the original sequence of permitted energy-values by another sequence of values located midway between them. I mention this chiefly in order to emphasize that the subdivision of phase-space into compartments is *ipso facto* quantum-theory.

As every reader knows, Planck postulated that the quantity b—the interval between the permitted energy-values, or the energy-range within a compartment, whichever picture is chosen—is the product of a universal constant (h) and the frequency of the oscillators (ν). The area of the equal compartments is then equal to the universal constant[7] whatever the frequency of the oscillators. From this latter statement the general principle is derived: To state it one must first adopt a symbol (say n) and a name (say *number of degrees of*

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[7] The point in the phase-space representing an oscillator of mass m, frequency ν, and amplitude C describes an ellipse having semi-axes C and $2\pi m\nu C$ and area $2\pi^2 m\nu C^2$; its energy is $U = 2\pi^2 m\nu^2 C^2$; hence the relation between energy U and area F is

$$U = \nu F$$

and the area between two ellipses is equal to h if the energy-difference between them is equal to $h\nu$.

freedom) for the number of distinct coordinates q required to describe the individual member of whatever assemblage one may be considering; this is also the number of distinct *momenta* p, there being one p for each q. Then the principle generalized out of Planck's postulate for oscillators is this: *For an assemblage of individuals with n degrees of freedom the phase-space is to be divided into compartments of volume* h^n.

We will now see what the classical statistics, supplemented by this principle, proposes for an assemblage of particles for which the relation between energy and momentum is $\epsilon = cp$ as it is for corpuscles of light, instead of $\epsilon = p^2/2m$ as it is for corpuscles of matter.

Different energy-values correspond as before to different spheres all centred at the origin of the momentum-space, but the numerical relations are changed. Instead of equations (24), we have:

$$\begin{aligned} \epsilon_s = cr_s, \qquad d\epsilon_s = cdr_s, \\ dV = 4\pi r_s^2 dr_s = (4\pi/c^3)\epsilon_s^2 d\epsilon_s, \end{aligned} \tag{36}$$

dV standing for the volume of the shell s covering the energy-range between ϵ_s and $\epsilon_s + d\epsilon_s$. Divide the momentum-space into compartments of equal volume H. We derive the "smoothed-over" distribution-function for the case in which N_i varies so little from one compartment to the next that even when the shell s is thick enough to comprise very many compartments the values of N_i for all of them may be equated to a mean value N_s. Under these conditions we may write for the number of compartments in the shell s,

$$Q_s = dV/H = (4\pi/c^3H)\epsilon_s^2 d\epsilon_s. \tag{37}$$

Putting down the classical value (15) for the number of particles in any of these compartments, remembering that N_i is identified with N_s, we obtain for M_s the number of particles in the shell s:

$$M_s = Q_s N_s = \alpha(4\pi/c^3H)\epsilon_s^2 e^{-\epsilon_s/kT} d\epsilon_s \equiv F(\epsilon_s)d\epsilon_s \tag{38}$$

and evaluate α by the same procedure as before. The result is:

$$F(\epsilon) = \frac{N}{3k^3T^3}\frac{\epsilon^2}{e^{\epsilon/kT}}. \tag{39}$$

This is the smoothed-over distribution-in-energy predicted for the radiation-gas by the classical statistics, it being assumed that the momentum-space is to be divided into compartments of equal volume. Experiment however supplies a quite different distribution-in-energy, to wit:

$$F(\epsilon) = \left(\frac{8\pi V}{c^3h^3}\right)\frac{\epsilon^2}{e^{\epsilon/kT} - 1}. \tag{40}$$

It looks as if (39) might be the limiting form of (40)—as if the actual distribution-law might be obtained by avoiding the approximations whereby we came to the formula (39), as Planck's law of distribution for oscillators was obtained by refraining from approximation. Such however is not the case. True, the second factor in (39) is evidently the limiting form, for very high temperatures, of the second factor in (40). But the first factor in (40) contains nothing but the volume of the gas and some universal constants, while the first factor in (39) contains the temperature and an apparently disposable constant standing for the number of particles in the assemblage. The former is not the limit of the latter. It will be noted also that although I said that the volume of the elements of phase-space was to be set equal to h^3, this assumption in no wise enters into the function (39). Bose in fact found it necessary to upset the basis of the classical statistics, in order to arrive at (40) instead of (39).

THE BOSE STATISTICS

The momentum-space of the photons is to be divided as heretofore into equal compartments, and various distributions of the particles among these are to be compared, in order that we may elect one of them as "the most probable" and make a picture of the entropy of the assemblage. But the manner of defining a distribution, the manner of "counting the ways" in which it may be realized and computing its "probability," is to be changed, and changed in a most thoroughgoing and fundamental way.

Start with any distribution of the particles, defined as heretofore: defined that is, by saying that there are N_0 of the particles in the compartment 0, N_1 in the compartment 1, and in general N_i in the compartment i.

Count the number of compartments containing no particle; call it Z_0. Count the number of compartments containing one particle apiece; call it Z_1. In general, let Z_i stand for the number of compartments containing i particles apiece. Put down the values of all the numbers Z_i.

Now change the terminology. Elect some neutral word, "arrangement" say, to denote what we have heretofore denoted as a "distribution," and use the latter word in the following new sense: a *distribution* shall henceforth be described by stating the values of the numbers $Z_0, Z_1, Z_2, \cdots, Z_i, \cdots$ and the total energy of the assemblage.[8]

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[8] It is of course confusing thus to change the meanings of words, but in the long run less confusing (I think) than to use some other word than *distribution* for the concept always called by that name in the new statistics.

This means that each distribution in the new sense comprises a number of distinct distributions in the old sense. This we shall regard as the number of different ways in which the distribution in the new sense may be realized. Going over entirely to the new terminology: we shall now identify the probability W^* of a distribution with the number of arrangements which are included in it. Previously we identified the probability W of an arrangement with the number of permutations included in it, according to equation (7). This we now must forget; we must proceed as if the probability of each arrangement were the same.

The number W^* is now to be evaluated. In doing this we must remember that we have to count, not the total number of arrangements yielding the prescribed set of values of the quantities Z_i, but the portion of these which give the prescribed value to the total energy of the assemblage.

As before, we superpose upon the partitioning of the momentum-space into small compartments of equal volume H, another partitioning into spherical shells each of which is sufficiently large to contain many of the compartments, yet sufficiently small so that the same value of ϵ may be assigned to all the compartments within it. The final result is thus to be a "smoothed-over" formula. It is rather singular that whereas Planck introduced the quantum into physics by avoiding the smoothing-over which had been customary in the classical statistics the quantum-formula for radiation is now derived by a method in which it is accepted.

Consider then any shell at random, say the "shell s." Denote by Q_s or by Z the total number of compartments in it; by Z_{is} the number of these compartments which contain i particles apiece; by M_s the number of particles in the shell. According to the scheme now being tried out, the number of ways of attaining the particular distribution characterized by the numbers Z_{is} is given by the formula:

$$W_s^* = \frac{Q_s!}{Z_{0s}!\,Z_{1s}!\,Z_{2s}!\cdots}, \qquad Q_s = \sum_i Z_{is}. \tag{41}$$

As the energy-values for all the compartments in the shell are (by hypothesis) approximately the same, these various ways of attaining the distribution Z_{is} all corresponding to approximately the same total energy, as well as the same total number of compartments and the same total number of particles.

Suppose this process repeated for every one of the shells s. The total number of ways of attaining the actual distribution, compatible with the conditions of constancy of total energy, total number of particles and total number of compartments, is then the product of all the quantities W_s^*: call it W^*:

$$W^* = \prod_s W_s^*. \tag{42}$$

As before, and with the same end in view, we form the expression for $\log W^*$, and employ Stirling's formula (assuming thus in effect that none of the quantities Z_{is} is smaller than ten or so):

$$\log W^* = \sum_s \log W_s^* = \sum_s [Q_s \log Q_s - \sum_i Z_{is} \log Z_{is}]. \tag{43}$$

We now take the very great step of *identifying* not $\log W$ of equation (10), but $\log W^*$, *multiplied by a constant k, with the entropy of the assemblage.*

$$S = k \log W^*. \tag{44}$$

Then, when the numbers Z_{is} are changed by small amounts δZ_{is}, the ensuing change δE in the total energy E of the assemblage must be linked to the ensuing change in $(k \log W^*)$ by the equation:

$$\delta S = \delta(k \log W^*) = \delta E/T. \tag{45}$$

The first variation of $(k \log W^*)$ is given thus:

$$\delta(k \log W^*) = -k \sum_s \sum_i (1 + \log Z_{is}) \delta Z_{is}. \tag{45a}$$

Let us try the distribution:

$$Z_{is} = \alpha_s e^{-i\epsilon_s/kT}. \tag{46}$$

Substituting this expression into (45a), we get:

$$\begin{aligned}\delta(k \log W^*) &= -k \sum_s \sum_i (1 + \log \alpha_s - i\epsilon_s/kT) \delta Z_{is} \\ &= -k \sum_s (1 + \log \alpha_s) \sum_i \delta Z_{is} + \frac{1}{T} \sum_s \epsilon_s \sum_i i \delta Z_{is} \\ &= \delta E/T,\end{aligned} \tag{47}$$

for the summation $\sum_i \delta Z_{is}$ vanishes because the number of compartments in each shell is invariable, while the quantity $\epsilon_s \sum i Z_{is}$ is equal to the total energy of the particles in the shell s.

The new statistics, in proposing a new conception of entropy as embodied in equation (44), therefore leads to a new distribution for thermal equilibrium. This distribution is expressed by equation (46) in the new-fashioned way, by stating the number of compartments in each shell which contain each of the permissible quotas of particles. We must translate it into a distribution-function-in-energy such as we used to express the results of the old statistics.

Before undertaking this translation, we compute the values of the constants α_s by summing the numbers Z_{is} over all values of i for each shell separately, and equating the sum to the total number Q_s of compartments in the shell. We obtain:

$$Q_s = \sum_i Z_{is} = \alpha_s \sum_i e^{-i\epsilon_s/kT} = \alpha_s(1 - e^{-\epsilon_s/kT})^{-1}. \tag{48}$$

On substituting these values of α_s into (46) we get something which begins to look familiar.

Next for the number M_s of the particles in the shell s, we compute:

$$\begin{aligned} M_s &= \sum_i iZ_{is} = \alpha_s e^{-\epsilon_s/kT}(1 - e^{-\epsilon_s/kT})^{-2} \\ &= Q_s \frac{1}{e^{\epsilon_s/kT} - 1}, \end{aligned} \tag{49}$$

which begins to look very familiar indeed.

Now for Q_s, the number of compartments in the shell s, we put the value already stated in equation (37), derived from the assumption that the compartments are all of the same volume H:

$$M_s = \frac{4\pi}{c^3 H} \frac{\epsilon_s^2}{e^{\epsilon_s/kT} - 1} d\epsilon_s \equiv F(\epsilon_s) d\epsilon_s. \tag{50}$$

Here the function $F(\epsilon_s)$ is the "smoothed-over" distribution-in-energy in which the new statistics culminates. Unlike those which we earlier derived from the old statistics, it involves the volume of the elementary compartments directly. Whereas from the old statistics we obtained formulæ involving the quantum only by avoiding the approximation, here we obtain a quantum-formula even when we admit the approximation—a contrast on which, I think, it is worth while to insist.

Let us then, in preparing for the final assumption, accept the principle generalized from Planck's assumption about oscillators: let the elementary cell of phase-space be given the volume h^3. This is not yet an assumption about the compartment of momentum-space. Supplement it, then, by supposing that the compartment of phase-space h^3 is the product of the compartment H of momentum-space and the entire volume V occupied by the radiation-gas. Then:

$$H = h^3/V. \tag{51}$$

This assumption—let me remark in passing—takes a very elegant form if we replace the compartments by the permitted energy-values, and then the corpuscular picture by the wave picture; for then we have a series of permitted wave-lengths, which are precisely those which can form stationary waves in a cube of volume V.

So the new statistics leads to the distribution-law:

$$F(\epsilon)d\epsilon = \frac{4\pi V}{c^3h^3}\frac{\epsilon^2}{e^{\epsilon/kT}-1}d\epsilon. \tag{52}$$

Dividing out the factor V, we get the number of particles per unit volume having energy-values between ϵ and $\epsilon + d\epsilon$, in an assemblage having the most probable distribution at the temperature T. Multiplying this by ϵ, we get the total energy per unit volume in the possession of such particles. Identifying these particles with photons, we observe that they have wave-lengths between ch/ϵ and $ch/(\epsilon + d\epsilon)$, frequencies between ϵ/h and $(\epsilon + d\epsilon)/h$. Transforming then from the variable ϵ to the new variables λ and ν, we obtain distribution-functions which give the *density of radiant energy* as functions of wave-length and frequency. It turns out that these agree absolutely with the observed distributions, except that they lack a factor 2. This factor is at once imported, and is ascribed to the fact that light is polarizable. So we arrive at the black body radiation-formula:

$$\rho(\nu)d\nu = \frac{8\pi h}{c^3}\frac{\nu^3 d\nu}{e^{h\nu/kT}-1} \tag{53}$$

and the new statistics is justified by its success.

It will be observed that the new statistics leads to a precise value for the number of photons per unit volume, at any prescribed temperature; whereas the old statistics led to nothing of the sort, but to a formula which contained the number of atoms per unit volume as a disposable constant. This corresponds to a profound physical difference between radiation-gas and material gases. When I state the temperature and the volume of a box containing helium, I am not giving data enough to fix the quantity of helium inside the box; on the contrary, the quantity and the density of the helium in the box can be varied *ad libitum* while the temperature and the volume are held constant. But when I state the temperature and the volume of an enclosure containing radiation, I am giving data sufficient to fix the amount of radiant energy and the number of quanta in the enclosure absolutely. This is a fact of experience, and the new statistics is evidently in accord with it. But if one were tempted to try out the new statistics upon a material gas, would there be any way of avoiding the inadmissible conclusion that the number of atoms in such a gas is also absolutely fixed by temperature and volume?

There is such a way. One might replace the distribution proposed in equation (46) by a more general one involving a disposable constant B, as follows:

$$Z_{is} = \alpha_s e^{-iB - i\epsilon_s/kT}. \tag{54}$$

On substituting this into the expression for ($k \log W$) we get instead of (47) the equation:

$$\delta(k \log W^*) = -k\sum_s(1 + \log \alpha_s)\sum_i \delta Z_{is} + kB\sum_s\sum_i i\delta Z_{is} + \frac{1}{T}\sum_s \epsilon_s \sum_i i\delta Z_{is}. \tag{55}$$

The right-hand member must as before reduce to $\delta E/T$ if the distribution (54) is acceptable; and this it will do, provided that not only $\sum_i \delta Z_{is}$ but also $\sum_s\sum_i i\delta Z_{is}$ is zero. Now the second of these quantities is zero for all variations in which the total number of particles remains the same. The distribution (54) enjoys a greater entropy than any other which is compatible with the same total energy and the same total number of particles. The distribution (46) was still more exalted; it enjoyed a greater entropy than any other compatible with the same total energy, even including those for which the total number of particles was somewhat different. But the distribution (54) is sufficiently distinguished to be qualified as the most probable distribution for a material gas. It seems rather singular that the distribution (46) is required for radiation-gas. Here is evidently one of the deep differences between matter and radiation.

Following the same routine as before, we arrive at the following expression for the number of particles in the shell s:

$$M_s = Q_s \frac{1}{e^{B+\epsilon_s/kT} - 1}, \tag{56}$$

and in dealing with radiation-gas we have put $B = 0$ and have taken the value of Q_s from equation (37). If in dealing with a material gas we take the value of Q_s from equation (25) instead and put $H = h^3/V$ we obtain:

$$M_s = \frac{2V}{h^3(\pi)^{1/2}}(2\pi m)^{3/2}\frac{(\epsilon_s)^{1/2}d\epsilon_s}{e^{B+\epsilon_s/kT} - 1} \equiv F(\epsilon_s)d\epsilon_s, \tag{57}$$

and now it is obvious that we must evaluate B in terms of the total number of particles N by the already so familiar way of integrating $F(\epsilon_s)$ over the entire energy-range from 0 to ∞ and setting the integral equal to N.

Einstein proposed this as an alternative to the Maxwell-Boltzmann law derived from the classical statistics. It is not easy to decide which of the two is supported by experiment, as with increasing temperature the formula (57) becomes more and more nearly like the classical one, and it turns out that throughout the convenient ranges of temperature and pressure the two are indistinguishable. It would be very valuable to determine between the two, as then we should know which of the two ways of defining a distribution and estimating the probability thereof, which of the two pictures of entropy, is the proper one for a material gas. The reader may have remarked that if one were to apply Bose's method to the problem of determining the most probable distribution of particles in ordinary space, one would reach a result at variance with that of the classical statistics, and therefore at variance with intuition. One must deal altogether with the six dimensional phase-space, to be perfectly consistent. This is to be regretted.

THE FERMI STATISTICS

The statistics invented by Fermi, and later independently by Dirac, involves the same fundamental assumptions as that of Bose—the same manner of counting the ways in which a distribution may be realized, of defining its probability, of picturing its entropy. But there is an additional assumption, of the nature of a limitation: it is postulated, that a compartment may contain not more than some specific maximum number of particles. In particular for a gas to which no external field is applied, it is postulated that each compartment must either be empty, or else contain one particle only.

The "exclusion-principle of Pauli" gave the hint from which the Fermi-Dirac theory sprang. This principle may be paraphrased as follows. In Bohr's "atomic theory of the atom" the electrons belonging to an atom are forbidden to revolve in any except certain specific orbits, set apart from the rest as the "permitted" orbits, and labelled by specific "quantum-numbers." In later versions of the theory the "permitted orbits" are less conspicuous, the "permitted quantum-numbers" more so; but the picture is acceptable at all events as a beginning. Upon this prohibition, then, Pauli superposed another; not more than one electron is allowed in each orbit or to each set of quantum-numbers. Perhaps it would be better to say "not more than some definite small number of electrons . . ."

instead of "not more than one." The affinity of this to one of Fermi's assumptions will soon be manifest. It would take much too long to give an idea of the successes of the Pauli principle; they are however so great as to increase the inherent plausibility of Fermi's idea very much—or perhaps I should say, so great as to render the idea plausible, which otherwise it might not seem.

The reasoning follows exactly the same course as when we were deriving the distribution-law (56), except that all the summations over the variable i are now summations of two terms only, the term for $i = 0$ and the term for $i = 1$. For each of the shells there are only two numbers Z_{is} required to describe the distribution: viz. Z_{0s} the number of empty compartments and Z_{1s} the number of compartments containing one particle apiece. We try the distribution (54):

$$Z_{0s} = \alpha_s; \qquad Z_{1s} = \alpha_s e^{B-\epsilon_s/kT}, \tag{58}$$

and easily find that it is the distribution of maximum probability, by comparison with all the others compatible with the same total number of particles and the same total energy. We arrive then at the following expression for the number of particles in the shell s:

$$M_s = Q_s \frac{1}{e^{B+\epsilon_s/kT} + 1}\cdot \tag{59}$$

There is no point in putting for Q_s the value appropriate to radiation-gas, since the Bose formula has already proved adequate for that case. Fermi put the value appropriate to material gases, and obtained:

$$M_s = \frac{2V}{h^3(\pi)^{1/2}}(2\pi m)^{3/2}\frac{(\epsilon_s)^{1/2}d\epsilon_s}{e^{B+\epsilon_s/kT}+1} = F(\epsilon_s)d\epsilon_s. \tag{60}$$

This formula is the point of departure for the theory of the electron-gas in metals revived and remodelled by Pauli and Sommerfeld, to the experimental tests of which most of the rest of this article will be devoted.

APPLICATION OF THE FERMI STATISTICS TO THE ELECTRONS IN METALS

We are asked to conceive of a piece of metal as a region populated with "free" electrons, and surrounded by a wall; the electrons being distributed according to the formula of Fermi.

The Fermi distribution-function involves the total number N of the electrons, which is a disposable constant. It also involves the volume V which this assemblage of N particles pervades. For this we set the volume of the piece of metal—a decision which is tantamount to ignoring the atoms, to supposing the metal a vacuum inhabited by free electrons only. So remarkable an assumption, even though it be made only in approximation, requires some excuse. Its strangeness may be mitigated by recalling, first, that slow electrons may go through atoms (at least through certain kinds of atoms) as imperturbably as if the atoms were not there; and second, that a wave-train may go without being scattered at all through a crowd of particles individually quite able to scatter it, provided that the particles are arranged in a regular lattice having a spacing smaller than the wave-length of the waves. The speeds attributed to electrons in metals are so low and their wave-lengths are so great, that perhaps they do behave in such a way.

The "wall" is the agency which prevents the electrons from escaping; it is commonly imagined as a sharp and sudden gradation of potential at the surface of the metal. Any electron moving towards it from within, with a velocity of which the component normal to the bounding surface may be denoted by u, is supposed to be driven back into the body of the metal if the corresponding "component of kinetic energy" $\frac{1}{2}mu^2$ is less than a certain constant W_a; while if $\frac{1}{2}mu^2 > W_a$ the electron escapes, but with its kinetic energy diminished by W_a. According to newer ideas electrons may sometimes escape even when their values of $\frac{1}{2}mu^2$ are smaller than W_a, and may sometimes fail to escape in the contrary case; but the earlier and simpler conception remains approximately valid, and I will abide by it for a time. The constant W_a may be named the *work-function.*

Like the constant N, the work-function figures as a disposable constant in the theory. It is an ambition of physicists to explain as many as possible of the differences between different metals, by varying only the values of these two constants. Later we shall find it necessary to introduce others, beginning with the one which in the older theories appeared as the mean free path of the electrons; but there are several results of value which can be obtained with no other but these two.

I repeat now from (60) the Fermi formula for the distribution-in-energy of an assemblage of N particles in volume V at temperature T, with two changes made to bring the notation into harmony with that of Sommerfeld:

$$F(\epsilon) = G\frac{2}{(\pi)^{1/2}}\frac{V}{h^3}(2\pi m)^{3/2}(\epsilon)^{1/2}\frac{1}{A^{-1}e^{\epsilon/kT}+1}. \qquad (61)$$

Here the symbol $1/A$ replaces e^B, and a factor G to which we shall assign the value 2 is introduced for a reason which will be stated later. The corresponding distribution-function in the coordinates and momenta is this:

$$f(x, y, z, p_x, p_y, p_z) = \frac{G}{h^3}\frac{1}{A^{-1}e^{\epsilon/kT}+1}\cdot \tag{62}$$

The first step now is the same as in the classical statistics: to determine the constant A in terms of N by integrating $F(\epsilon)$ over the whole range of energy-values from 0 to ∞, and equating the integral to N:

$$\int_0^\infty F(\epsilon)d\epsilon = N. \tag{63}$$

This was an easy step in the classical statistics, but here it is very hard. The integral of $F(\epsilon)$ is not one of the common well-known functions to be found in mathematical tables, nor a combination of such; and we do not get a simple equation to be solved for A in terms of N. Sommerfeld indeed found it necessary to compromise by deducing two series-expansions for the integral, one being available for values of A smaller than unity, the other for the opposite extreme. By a stroke of luck which seems almost too good to be true, the first one or two terms of one or the other of these expansions form an approximation amply good enough for all the cases where as yet theory and experiment can be compared.

I consider first the approximation which is of *no* importance in the theory of electrons in metals—the one for values of A so very small that the second term in the denominator of $F(\epsilon)$ is negligible by comparison with the first. Then the distribution-law approaches that of Maxwell and Boltzmann, and of necessity the constant A must possess the value which in the limit makes $F(\epsilon)$ identical with the classical expression written in equation (27): to wit, the value:

$$A = \frac{Nh^3}{GV}(2\pi mkT)^{-3/2}. \tag{64}$$

It would however be a great error to suppose that this value of A can be substituted into the function F under all circumstances. This value is acceptable only if A is very small relatively to unity, which is to say, if the quantity to which A is here equated is very small. So the question arises: in any physical case, is the combination on the right-hand side of equation (64) a small fraction of unity, or is it not?

Now for any material gas under any conditions usual in the laboratory, A is indeed very small. The new statistics leads to a result indistinguishable from that of the old statistics. To discriminate between the two by experiments on material gases, one would have to work with temperatures so low and densities so high that the gases would probably either be liquefied already, or at least would be in a condition very different from that "ideal" state to which the statistics is tacitly supposed to apply. Perhaps though it is not impossible to make the test with helium or hydrogen.

A this point apparently Fermi stopped. But it occurred to Pauli that if the new statistics were applied to an electron-gas as dense as that which Riecke and Drude had supposed to pervade the interiors of metals, the deviations from the classical distribution would be much more pronounced. For, in the first place, the mass m of the individual electron is smaller by several orders of magnitude than the mass of the atoms or molecules of any material gas. And, in the second place, if the number N of free electrons in a piece of metal is as great as or greater than the number of atoms, then it is thousands of times as great as the number of particles in an equal volume of a material gas. Now the quantity equated to A in equation (64) contains N in the numerator and $m^{3/2}$ in the denominator, and for the hypothetical electron-gas within the metals it is no longer small. The expression (64) for A is then no longer acceptable.

While the statement just made about m is based on a fact of experience, the statement about N is not so firmly grounded. We have no direct knowledge of the number of free electrons in a given volume, say the number n $(= N/V)$ in unit volume, of a metal. This as I said above is a disposable constant of the theory. One of the tests of the theory is whether one can obtain correct numerical values of half-a-dozen properties of a metal by choosing a single value of n for that metal. So long as the classical statistics was applied to the electron-gas, this was impossible. If the value of n was put as high as the number of atoms in unit volume, the predicted value of specific heat (and we may now add, the predicted value of susceptibility) turned out to be too large; if n was lowered sufficiently to avoid this particular discordance, other predictions were impaired. It was however the general impression, that one should put n equal to the number of atoms or a small multiple thereof. I suspect that this decision was largely due to a feeling that since the free electrons are detached from atoms, and since all the atoms are alike, any atom should supply as many free electrons as any other. However that may be, it was natural though not inevitable for Pauli and for Sommerfeld to link the Fermi statistics with the postulate that there are as many free electrons as there are atoms, and test the combination of these two assumptions.

On putting for m the mass of the electron, for N/V the number of atoms per unit volume of any metal, for T any temperature from zero absolute up to several thousand degrees, and for G any small integer, one finds that the quantity equated to A in (64) is very large. Thus with $N/V = 5.9 \cdot 10^{22}$ (the number of atoms in a cc. of silver), $T = 300°$ K., $G = 2$, Sommerfeld computed:

$$(nh^3/G)(2\pi mkT)^{-3/2} = \text{about } 2400 \tag{65}$$

a result which invalidates equation (64).

We turn then to the other series-expansion of the integral $\int F(\epsilon)d\epsilon$, the one which Sommerfeld proved applicable for large values of A. The first two terms of this expansion are as follows:

$$\int_0^\infty F(\epsilon)d\epsilon = N = \frac{GV}{h^3}\frac{4\pi}{3}(2mkT\log A)^{3/2}\left(1+\frac{\pi^2}{8}(\log A)^{-2}+\cdots\right)\cdot \tag{66}$$

Taking the first term only of this expansion and putting the aforesaid values of N/V and T and solving for $\log A$, one finds a very large value indeed ($\log_e A = 325$). Assuredly then we may use the first two terms of this expansion by themselves when we are dealing with the electron-gas in a metal, and indeed the first term will for some purposes be amply sufficient.

We have thus the following first—and second—approximation formulæ for A in terms of n or N/V:

$$\begin{aligned} 2mkT\log A &= h^2(3n/4\pi G)^{2/3} \qquad \text{first approx.} \\ 2mkT\log A &= h^2(3n/4\pi G)^{2/3}\left[1 - \frac{(2\pi mkT)^2}{12h^4}\left(\frac{3n}{4\pi G}\right)^{-4/3}\right] \\ &\qquad\qquad\qquad \text{second approx.} \end{aligned} \tag{67}$$

(the second approximation being computed by putting the first-approximation value of $\log A$ into the second term of the series expansion).

On substituting one or the other of these into the distribution-functions (61) and (62), we have the postulated distribution of the free electrons expressed to as high a degree of approximation as we require, with no disposable constant except n; and we are ready for the applications.

The Specific Heat

As it was the notorious difficulty with the specific heat which spoiled the old electron-gas theory in which the classical statistics was coupled with the assumption that there are as many free electrons as atoms, let us first of all find out whether this difficulty remains.

Any distribution-law for an assemblage leads immediately to a formula for the total energy E thereof as function of the temperature, which is:

$$E = \int_0^\infty \epsilon F(\epsilon) d\epsilon. \tag{68}$$

Putting the distribution-in-energy (27) derived from the classical statistics, we find:

$$E = \frac{3}{2} NkT \tag{69}$$

and putting the one just derived from the Fermi statistics with the first-approximation value of A, we find:

$$\begin{aligned} E &= E_0 + \tfrac{1}{2}\gamma VT^2, \\ E_0 &= \frac{2\pi}{5}\frac{VGh^2}{2m}\left(\frac{3n}{4\pi G}\right)^{2/3}, \\ \gamma &= \frac{\pi}{3} mG \frac{(2\pi k)^2}{h^2}\left(\frac{3n}{4\pi G}\right)^{1/3}, \end{aligned} \tag{70}$$

two exceedingly different formulæ.

The derivatives dE/dT of these expressions are the formulæ supplied by the two statistics for the specific heat of the electron-gas. The classical theory predicts for the specific heat a constant value, while the Fermi statistics makes it proportional to the temperature—being thus in harmony with Nernst's heat theorem, while the other is not—and gives it even at room temperatures but a small fraction of the classical value.

Experimentally the specific heat of the electron-gas cannot be measured separately from that of the lattice of atoms, which constitutes the metal—an admission which seems to condemn as vain all hope of testing these formulæ. Nevertheless one can conclude with fair certainty that the classical expression is inadmissible; for the specific heat of an ordinary metal agrees so well with the value attributed by statistical theories both old and new *to the atoms alone*, that there is simply none left over for the electrons—no such great excess, that is to say, as the amount $3nk/2$ which the classical theory requires. The device of reducing n to so low a value that $3nk/2$ would be inappreciable makes trouble in other directions, as I have intimated. But with the new statistics the theoretical value γVT is inappreciable even when n is made as great as the number of the atoms and T as great as many hundreds of degrees. Probably no one who did not often lament the defeat of the old and so very desirable electron-gas theory by that hard fact about the specific heat will ever quite realize the rejoicing caused by this victory of the new, which by this achievement succeeded *a se faire pardonner* many deficiencies in other fields.

Features of the Fermi Distribution

I will now mention some of the features of the Fermi distribution which has thus justified itself by passing its first test.

The most startling of these may be inferred from the distribution-function (62) or (61), by inserting the first-approximation formula for A presented in equation (67), and a new symbol W_i:

$$f = \frac{G}{h^3}\frac{1}{e^{(\epsilon - W_i)/kT} + 1}; \qquad W_i = \frac{h^2}{2m}\left(\frac{3n}{4\pi G}\right)^{2/3}. \tag{71}$$

At the absolute zero the exponential term is either infinity or zero, according as the variable ϵ is greater or less than W_i. Therefore the density of the electrons in phase-space is constant and equal to G/h^3 for all energy-values less than W_i, zero for all values of energy greater than W_i.

This striking result can easily be deduced from Fermi's basic assumption, without any statistics at all. Absolute zero is by definition the temperature of the state, being in which the assemblage can give away no energy whatever. If not more than one electron may occupy any compartment of the phase-space, absolute zero is attained when there is an electron in every compartment from the origin outwards to a sphere which is centered at the origin, and which has just the volume needful to contain as many compartments as there are electrons. The number of electrons in unit volume of the phase-space is and remains equal to the number of compartments in unit volume, *i.e.* to the reciprocal of the volume of the elementary compartment, from the origin outward to this sphere; there it suddenly sinks to zero, and so continues. Cooling-down of an assemblage is settling-down of the particles into this the most condensed of all permissible arrangements; it is like crystallization upon a lattice, only the lattice is in the phase-space.

The foregoing statements may all be repeated, with the words *phase-space* replaced by *momentum-space*. In the momentum-space, a sphere of radius p, consequently of volume $4\pi p^3/3$, contains $(4\pi p^3/3)/(h^3/V)$ of the elementary compartments. If we set this number equal to the total number of electrons N, and solve the resulting equation for p, we get the radius of the sphere which would just contain all the electrons if there were one in each compartment. If we set the volume of the sphere equal to Nh^3/VG and solve for p, we get the radius p_m of the sphere which would just contain all the electrons if there were G of them in each compartment. But this is the maximum value of the momentum of the electrons, it is the momentum of the fastest of the electrons. The corresponding speed v_m of the fastest of the electrons is p_m/m, therefore is given by the expression:

$$v_m = \frac{h}{m}\left(\frac{3n}{4\pi}\right)^{1/3} \tag{71a}$$

and the corresponding kinetic energy $\frac{1}{2}mv_m^2$ is the same as W_i.

It is expedient to set down for future reference the *mean values* of speed v and of several integer powers of v, for a gas distributed according to the Fermi law at the absolute zero. The general formula for the mean value of any power v^s of v is this:

$$\overline{v^s} = \frac{1}{n}\int v^s f(v)dv = \frac{1}{n}(4\pi G/m^3h^3)\int_0^{v_m} v^{s+2}dv$$

and in particular:

$$\overline{v^{-1}} = 3/2v_m; \qquad \bar{v} = 3v_m/4; \qquad \overline{v^2} = 3v_m^2/5; \qquad \overline{v^3} = \tfrac{1}{2}v_m^3. \tag{72a}$$

The corresponding values for the Maxwell distribution are these:

$$\begin{aligned} \overline{v^{-1}} &= 2(m/2\pi kT)^{1/2}; & v^2 &= (2kT/m); \\ \bar{v} &= 2(2kT/\pi m)^{1/2}; & \overline{v^3} &= 4\pi(2kT/\pi m)^{3/2}. \end{aligned} \tag{72b}$$

Plotted as functions of ϵ, the distribution-function f in the coordinates and momenta starts out as an horizontal straight line at a distance G/h^3 from the axis of abscissæ, while the distribution-function F in the energy starts out as a concave-upward parabolic arc; these continue as far as the abscissa $\epsilon = W_i$, and from then on the curves coincide with the axis of abscissæ.

The foregoing statements are valid for absolute zero; what happens as the temperature rises? Sommerfeld has proved that the sharp angles in the distribution-curve are *very gradually and slowly* rounded off, the curve always traversing the midpoint of the vertical arc BC (Fig. 1). The far end of the curve sinks down to the axis of abscissæ in the fashion of the Maxwell law. Even at room-temperature and even far above, however, the distribution departs so little from the absolute-zero form that many phenomena may be interpreted in a qualitative way, simply by imagining the absolute-zero distribution—the completely degenerate distribution, it is called—to persist all through the observable range of temperatures. Indeed, in calculating electrical resistance and certain other properties of metals, one may use the mean values of the various powers of v which are tabulated in (72*a*). There are however other properties of metals, thermal conductivity for instance, for the estimation of which it is not sufficient to assume that the mean values of the powers of v are always the same as at absolute zero, and one must derive more nearly approximate values for them; for these however I refer the reader to Sommerfeld.

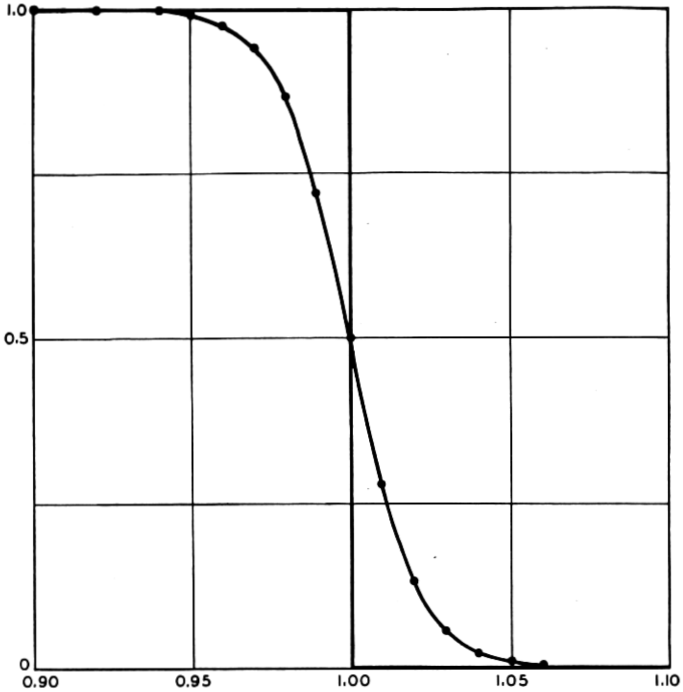

Fig. 1—Graphs of the Fermi distribution-function f plotted against ϵ/W_i as independent variable, for an electron-gas having $6.5 \cdot 10^{22}$ particles per cc., at temperatures zero (rectilinear curve) and 1500° K. (rounded curve). The value of W_i is 6 equivalent volts.

In practice, the values of W_i are rather astonishingly great; no less, for example, than 5.6 equivalent volts for silver, 5.7 for tungsten, 6.0 for platinum. Obviously they depend on the compactness of the lattice, being greater the more closely-packed the atoms are. In potassium and sodium the atoms are relatively widely spaced, and the corresponding values of W_i are about 2.1 and 3.2 in equivalent volts.

The contrast between this and the classical situation is evidently enormous. Where formerly we were asked to think of the electrons in a metal at usual temperatures as being distributed Maxwell-wise about a very modest mean energy, say about 0.02 of an equivalent volt, we are now invited to conceive them as distributed all through a range of energies extending from zero up to as much as half a dozen equivalent volts, and more abundantly the nearer one approaches to the top of this range, abruptly though the distribution ceases when the very top is reached. This is "zero-point energy" with a vengeance!

The pressure of the electron-gas is related to the energy-per-unit-volume by the equation valid also in the classical theory:

$$p = \frac{2}{3}\frac{E}{V},$$

and therefore varies like the total energy—starting from a value absurdly high at the absolute zero (hundreds of thousands of atmospheres) and increasing therefrom very slowly at first, though according to a T^2 law, as the temperature rises. I do not know of any manometer for measuring internal electron-pressures, but if anybody should invent one he had better make it strong.

There is manifest ground for doubting these remarkable proposals: thermionic data seem to show that the work-function which opposes the egress of the electrons from a metal is itself less than half-a-dozen volts (in the usual measure), for some metals less than two—what then keeps these fast electrons confined within the metal? It turns out, however, that in augmenting the *vis viva* of the electrons the new theory also raises the top of the wall which they must overleap. Here indeed we meet with the first of the new experiments which tend to confirm the new theory.

Thermionic Emission

The simplest theory of the thermionic current is, that it consists of all the electrons belonging to the interior electron-gas which fly against the boundary-surface of the metal with velocities such that the component u thereof perpendicular to the boundary-surface is great enough to make the "energy-component" $\frac{1}{2}mu^2$ greater than a constant W_a—the said constant being interpreted as the work-function or the retarding potential-drop at the edge of the metal. The thermionic electrons are those which swim up to the surface with an outward-bound velocity-component so large, that by means of the kinetic energy of their outward motion they can climb over the wall.

Evidently any thermionic emission must distort the distribution of the electron-gas inside the metal, as it is an unbalanced outflow of electrons. The situation in which the efflux is balanced by a corresponding influx from an electron-gas outside the metal is much regarded in thermodynamic theory, but one cannot measure currents in that situation any more than one can measure heat-flow between two bodies at equal temperature. In assuming, then, that the distribution of the internal electrons is that of Fermi or that of Maxwell, we shall probably be invalidating our conclusions except for the limiting case of an infinitesimal emission. It seems probable, however, that with the thermionic currents of practice the approximation is good enough.

The simplest theory of the thermionic current, then, consists entirely of the equation:

$$i = e\left(\frac{m}{h}\right)^3 G \int_{w=u_0}^{\infty} du \int_{-\infty}^{\infty} dv \int_{-\infty}^{\infty} dw \cdot u \, \frac{1}{A^{-1}e^{\epsilon/kT} + 1} \cdot \qquad (73)$$

This is a restatement of the first sentence of this section, *plus* the assertion that even when electrons are leaking out through the wall of the metal the distribution within remains practically that of Fermi. The factor e stands for the electron-charge; the symbol i thus for the thermionic current-density in electrostatic units. The factor m^3 enters because, in conformity with usage, I have translated from the momenta into the velocity-components u, v, w as independent variables. The quantities u_0 and W_a are related by the equation:

$$W_a = \tfrac{1}{2} m u_0^2. \qquad (74)$$

In the integrand we are of course to put $\frac{1}{2}m(u^2 + v^2 + w^2)$ for ϵ.

Setting for A the first-approximation value from (107) with the symbol W_i defined in (71), we obtain:

$$i = e\left(\frac{m}{h}\right)^3 \int_{u_0}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u \, \frac{1}{e^{(\epsilon - W_i)/kT} + 1} \, du dv dw. \qquad (75)$$

The integration is perfectly straightforward if the second term in the denominator may be neglected relatively to the first. This seems unnatural, for we have just been noticing that over part of the energy-range, from $\epsilon = W_i$ downwards, the second term is larger than the first. But if W_a is considerably larger than W_i—and by this I mean, if $(W_a - W_i)/kT$ is positive and considerably larger than unity—then the electrons which escape are those which belong to the extreme upper part of the energy-range, where the first term is much the larger. Writing then $u \cdot \exp\left[-(\epsilon - W_i)/kT\right]$ for the integrand, we integrate with ease by well-known formulæ, and get:

$$i = \frac{2\pi emG}{h^3}(kT)^2 e^{-(W_a - W_i)/kT}. \tag{76}$$

The experimental test consists in plotting ($\log i - 2 \log T$) against $1/T$; we should get a straight line provided that W_a does not vary with temperature. The experiments do lead to precisely this result. The slope of the line varies from metal to metal, and depends on the state of the metal surface; identifying it with $(W_a - W_i)/k$, one finds that W_a exceeds W_i by amounts ranging from one equivalent volt upward to five or six; so the approximation just mentioned is abundantly justified, even up to temperatures of incandescence.

The contrast with the predictions of the classical theory is peculiarly interesting. Assuming the Maxwell distribution for the interior electrons, one arrives easily (the reader can do it by substituting the value of A from (64) into (73)) at the formula:

$$i = \frac{en}{(2\pi m)^{1/2}}(kT)^{1/2} e^{-W_a/kT}. \tag{77}$$

On testing this formula by plotting ($\log i - \frac{1}{2} \log T$) against $1/T$, it is found that the experiments yield lines as beautifully straight as those obtained by plotting ($\log i - 2 \log T$). Indeed—as everyone knows who has dabbled in thermionics—a function of the type $\exp(-c/T)$ varies so exceedingly rapidly with $1/T$ that it makes no perceptible difference to the graph whether or not the function is multiplied by a constant or by any modest power of T. One cannot then use the graphs to distinguish between the theories, even if one could be sure that W_a is not a function of T. But the classical theory proposes that we identify the slope of the aforesaid line with W_a/k; and it has been the custom so to do.

Now *if the Fermi distribution-function is the right one, physicists have been underestimating the work-function all along.* They have plotted experimental curves which agreed in shape with (76) and (77) and from these they have evaluated the constant figuring in the exponent, a constant which they have denoted usually by $-b/k$; and then they have equated b to W_a, whereas if it is right to apply the new statistics they should have added W_i to b and then equated the sum to W_a. Nor is the alteration slight: for if there are as many free electrons in the metal as there are atoms, then W_i is six volts or thereabouts, and the quantity to be added to the observed constant b is larger than b itself.

Is there then any other way of determining the work-function than out of this apparently ambiguous current-vs-temperature curve? If there is a direct and independent way, it may serve not only to decide between the two statistics, but also—if it favors the new by yielding a value for W_a greater than the thermionic b—to give an *experimental* value for $(W_a - b) = W_i$ and hence for the disposable constant n which is the one uncertain quantity in the theoretical formula for W_i. It may, that is to say, serve to determine the number of electrons per unit volume of the electron-gas.

Now it seems that the diffraction of electrons by crystals provides an independent and direct way of determining the work-function. For in the phenomena in which negative electricity behaves as a wave-motion, the work-function figures in the index of refraction; and the index of refraction of a metal may be determined from the diffraction-patterns which it forms when irradiated with slow electrons. Ample data concerning one metal—nickel—have already been acquired by Davisson and Germer, and from these it transpires that the work-function is much in excess of the thermionic constant b—so much indeed, that the corresponding value of W_i implies that there are twice as many free electrons as atoms in the metal, or even more.[9] The values deduced for the work-function from the refractive index vary however with the speed of the electrons; and it is evident that much remains to be understood.

The factor which multiples $T^2 \exp\left[-(W_a - W_i)/kT\right]$ in the right-hand member of (76) involves universal constants only (supposing that G is such) and is therefore the same for all metals—a principle derived by Richardson from the first and second laws of thermodynamics twenty years ago, without any assumptions at all about the distribution of the electrons. Its actual value $2\pi k^2 meG/h^3$ differs only by the factor G from the value derived by Dushman, which is numerically equal—in the customary units—to 60.2 amperes per cm.^{2} per degree squared. There are several metals for which the experimental value of this quantity—commonly known as A, a symbol which in this article is monopolized by another meaning—agrees well with 60.2. One might infer that G must be unity, a choice which would demolish the theory of paramagnetism; but there is another recourse; one may suppose that half the electrons which

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[9] L. Rosenfeld, E. E. Witmer (*l. c. infra*). From Rupp they cite values of refractive index for six other metals (Al, Cr, Cu, Ag, Au, Pb) and compute values of n. In considering these, however, the reader should assess G. P. Thomson's criticism of Rupp's values.

come up to the bounding surface from within with energy sufficient to escape are nevertheless reflected. A factor $(1 - r)$—r being called the coefficient of reflection, and being put equal to $\frac{1}{2}$—then enters into the formula, and balances out the factor 2 introduced by giving the preferred value to G. Moreover one may explain values of the constant still smaller than 60.2, or between 60.2 and 120.4, by adjusting r accordingly. But there are also recorded values enormously greater than 120; so evidently something remains to be understood.[10]

The methods of wave-mechanics have been applied by Fowler and Nordheim to the problem of evaluating this coefficient of reflection. They have attained some notable results in the fields of thermionics, cold discharge, and photoelectric effect. These however are consequences not of the new statistics only, but of a combination of the new statistics with the new way of considering the transmission and reflection of electron-waves at surfaces. There is not space for me to deal with the latter, beyond indicating its point of departure and its chief results.

Thus far I have been speaking of a metal as an equipotential region surrounded by a surface at which there is a sharp potential-drop, and beyond which there is the equipotential region of outer space. Fowler and Nordheim however, like Schottky and others before them, conceive a metal as an equipotential region surrounded by a surface, beyond which lies a region in which there is a field (or at all events an image-field) the strength of which is a function of the distance from the surface. The quantity W_a appears as the integral of this field-strength, from the surface to infinity. Electrons of a given kinetic energy being supposed to fall against the surface from within, the fraction which fails to pass completely through the region of the field depends upon the kinetic energy of the electrons and upon the *shape* (not solely upon the integral) of the field-strength-vs-distance curve. The average value of this fraction for all the electrons of all speeds coming up to the surface from within—the average being taken with due regard to the relative proportions of the electrons of various speeds, that is to the distribution-in-velocity—is the coefficient r aforesaid. For certain simple shapes of the field-vs-distance curve it may be calculated. One thus arrives at the be-

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[10] If the empirical equation is of the form $i = aT^n \exp(-b/T)$, then whatever may be the values of the constants a and b, one can always claim that it agrees with the foregoing theory provided one assumes that W_i or r or both vary with temperature in just the proper way. But, as Fowler puts it: "the variety of possible uncontrollable hypotheses (if such assumptions are to be admitted) becomes too large for profitable discussion."

ginnings of a theory of the effects of surface-conditions on thermionic-emission, and of the cold discharge.

The Cold Discharge

Suppose that a potential-difference is now applied between the metal and a neighboring electrode, such that near the metal the resulting field-strength is very great. Does it penetrate the region which I have just been describing? Assume that it does penetrate as far as the "surface" just defined. Then, everywhere beyond the surface, the actual field is the resultant of this "applied" and the previously-mentioned "intrinsic" field. The shape of the field-strength-vs-distance curve is thus changed, in a way which is calculable if we have postulated some particular original shape; and in certain simple cases it is possible to calculate the consequent change of the coefficient r, and therefore the electron-current—or the additional electron-current—which the applied field causes to emerge from the metal. This is the current known as the "cold discharge."

Nordheim adopted for the field-strength-vs-distance curve, in the absence of applied P. D., the shape which is most commonly proposed—the inverse-square curve, the law of the "image-force" which a charge in the vicinity of a conductor experiences because of its "electrical image" in the conductor. For the current i of the cold discharge he then derived this approximate formula:

$$i = c'SF^2 \exp\,(-\,c''/F), \tag{78}$$

in which F stands for the applied field, S for the surface-area of the metal exposed to it, c' and c'' for constants which can be calculated when W_i is known.

There are certain experiments (for an account of which I refer to Nordheim's paper in the Physikalische Zeitschrift) which indicate that the actual relation between the current and the field-strength agrees in form with (78), but that the predicted values of c' and c'' are too large—too large by a factor of the order of ten in the latter case, by several orders of magnitude in the former. However it is possible to explain away these contradictions. One may assume, for instance, that the actual surface concerned in the discharge is a collection of small spots which altogether have but a small fraction of the total area of the metal surface; and that over these small spots, the field-strength is much higher than it would be if the metal were everywhere uniform and smooth. The ratio of the observed to the predicted value of c' then gives the fraction of the total surface which is covered by these "active" spots, and the ratio of the observed to the predicted value of c'' gives the reciprocal of the factor by which the field-strength must be multiplied.

This explanation has the disadvantage of being not only plausible but much too easy. So long as there is not any independent evidence about the area of the effective spots or the field-strength prevailing over them, the theory simply delivers an equation with two disposable constants, which is not very valuable for testing the underlying assumptions. It appears from the data examined by Nordheim, however, that the ratio of the predicted to the observed value of c'' is always between 10 and 20, and the ratio of the observed to the predicted value of c' is always about 10^{-10} (at least for tungsten). This uniformity of the two quantities which figure in the theory as the disposable constants may be taken as a confirmation of some weight.

Photoelectric Effect

According to the former theory, the elementary process of the photoelectric effect runs thus: a quantum dives into a metal, and gives its whole energy (say E_0) to an electron initially at rest, which then may escape from the metal after suffering a reduction of kinetic energy equal at least to W_a and possibly more (more, that is to say, if the electron loses kinetic energy on its way to the surface). Even if we suppose that the electron originally belonged to an electron-gas conforming to the classical statistics, its initial energy would almost always be quite negligible compared to that which the quantum gives it. But if the electron-gas obeys the new statistics, it comprises electrons with energy-values ranging up to W_i. However if the new statistics is valid, then the reduction of kinetic energy at the boundary is also greater by W_i than we have hitherto supposed. The net result is, that by the new statistics as by the old we derive Einstein's equation for the maximum kinetic energy of the electrons expelled by quanta of frequency ν:

$$E_{\text{max}} = E_0 + W_i - W_a = h\nu + \text{const.} \tag{79}$$

only the additive constant is now $(W_i - W_a)$ instead of $(- W_a)$. This additive constant should as before agree with the thermionic constant b.

The new theory has one marked distinction, probably an advantage, over the old: it implies a sharply definite maximum kinetic energy—that is to say, the distribution-in-energy function of the escaping electrons should jump suddenly from zero to some definitely higher value at the energy-value $E = E_{\text{max}}$ prescribed by (79); the slope of the curve representing this function should make an acute angle with the axis of E where they intersect at $E_{\max}$. The Maxwellian distribution predicted by the classical statistics for the interior electrons suggests however that the curve in question should approach the axis asymptotically. The new statistics leads also to certain inferences about the shape of the curve for values of E less than $E_{\max}$. A great quantity of data bearing on this subject has been obtained by Ives and his collaborators; but the interpretation is made difficult by the presumption that some allowance must be made for the energy-losses suffered by electrons after they absorb quanta but before they reach the surface, and will require much study.

Paramagnetism of the Electron-Gas

The susceptibility of the electron-gas was calculated by Pauli even before the specific heat was evaluated by Sommerfeld, but as it involves an extra complication I have inverted the historical order.

The complication is due of course to that assumption which is made in order to explain why the electron-gas should be magnetic at all—the assumption that electrons are magnets. Perhaps I am too cautious in referring to it as an assumption, it being so well authenticated by the gyromagnetic effect and by the general usefulness of the "spinning electron" in the explanation of spectra. These phenomena impose a special value on the magnetic moment μ_0 of the electron, to wit, the value,

$$\mu_0 = eh/8\pi m_0 c, \tag{80}$$

m_0 standing for the rest-mass of the electron. Further they require that when the electron is floating in a magnetic field, its moment (considered as a vector) shall be either parallel or anti-parallel to the field. Denote by θ the angle between the moment of the electron and the magnetic field: then θ must be either 0 or π.[11] Now when a magnet of moment M is inclined at an angle θ to a magnetic field H, its "extra magnetic energy" is $- MH \cos \theta$.[12] In dealing with the electron-gas, then, we are in effect assuming that when a field H is applied to it the energy of every electron is either increased or decreased by the amount:

$$\Delta = ehH/8\pi m_0 c. \tag{81}$$

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[11] It comes to the same thing, and may on other grounds be preferable, to assign μ_0 twice the value given in (80), and to θ the values 60° and 120°.

[12] The magnetic energy, or energy due to the "interaction between the magnet and the field" is put equal to zero when the magnet is transverse to the field, which is consistent with the picture that the field alters the energy of the magnet by speeding up or slowing down the revolving electricity. The formula here given is a first approximation.

As I mentioned earlier, the idea of compartments in the momentum space may be replaced by the idea of "permitted energy-values," at least in some situations. Let us for convenience return to the latter conception. Then we may say that when a magnetic field is applied to an electron-gas of which the particles are magnets, each of the permitted energy-values is split into two. To any previously-permitted value ϵ correspond a pair of new ones, $\epsilon + \Delta$ and $\epsilon - \Delta$; or let me say $\epsilon + m\Delta$, using m as a symbol which may have only the values $+ 1$ and $- 1$.

Pauli assumed that the most probable distribution of the electrons among this doubled set of energy-values is to be determined by the new statistics, including Fermi's postulate so modified as to state that not more than one electron may possess any one of the permitted values.

Previously I used the symbol Z_{is} to denote the number of compartments or permitted energy-values which lie in the shell s and are occupied by i electrons apiece; and the symbol Q_s to denote the total number of permitted energy-values in the shell s. Now there are Q_s permitted values which are shifted upward by Δ from the original ones, and Q_s more which are shifted downward by Δ from the original ones. Let Z_{is+1} stand for the number in this upward-shifted group which are occupied by i electrons apiece, and Z_{is-1} for the corresponding number in the downward-shifted groups; Z_{ism} shall be the general symbol for the two.

Now consider the distribution:

$$Z_{ism} = \alpha_{sm} e^{-iB - i(\epsilon_s + m\Delta)/kT}, \qquad \begin{aligned} m &= +1, -1, \\ i &= 0, 1. \end{aligned} \tag{82}$$

This answers the standard requirements for thermal equilibrium. For if we define W^* in Bose's way, and then say that the entropy is $k \log W^*$, we find that when the energy of the assemblage is varied by δE—the total number of cells and the total number of particles remaining constant—the first variation of the entropy is $\delta E/T$, as it should be. I leave it to the reader to prove this statement as corresponding statements for other distributions (*e.g.* (47)) were earlier proved, and to determine the values of the quantities α_{sm}; on doing which, and substituting the results into this distribution, he should obtain

$$Z_{1s,\,+1} = \frac{Q_s}{e^{B+(\epsilon_s+\Delta)/kT} + 1}, \qquad Z_{1s,\,-1} = \frac{Q_s}{e^{B+(\epsilon_s-\Delta)/kT} + 1}, \qquad Q_s = \frac{2}{(\pi)^{1/2}} \frac{V}{h^3} (2\pi m)^{3/2} (\epsilon_s)^{1/2}. \tag{83}$$

It is best, perhaps, to regard these formulæ as the descriptions of two electron-gases, one composed entirely of magnets parallel to the field, the other of anti-parallel magnets; the actual electron-gas is a mixture of the two. The quantity $Z_{1s,\,-1}$, for example, is the number of parallel magnets having energy-values shifted downwards through Δ from the Q_s originally-permitted energy-values which lay in the shell s. True, these magnets are no longer themselves in the shell s, owing to the shift; their energies lie between $(\epsilon_s - \Delta)$ and $(\epsilon_s - \Delta + d\epsilon_s)$, not between ϵ_s and $\epsilon_s + d\epsilon_s$; but for ease of integration it is better to think of them as being associated with the original unshifted energy-values. The total number of magnets comprised in the parallel gas is then given by the equation:

$$N_1 = \frac{2}{(\pi)^{1/2}} \frac{V}{h^3} (2\pi m)^{3/2} \int_0^\infty \frac{(\epsilon)^{1/2} d\epsilon}{e^{B+(\epsilon-\Delta)kT} + 1} \cdot \tag{84}$$

For brevity denote by L the constant before the integral; and use the symbol ϕ for the function defined as follows:

$$\phi(u) = \int_{\epsilon=0}^\infty \frac{(\epsilon)^{1/2} d\epsilon}{e^{\mu+\epsilon/kT} + 1} \cdot \tag{85}$$

Then expanding N_1 as a power-series in the variable Δ/kT which is $\mu_0 H/kT$, we find:

$$N_1 = L\left[\phi(B) - \frac{\mu_0 H}{kT}\phi'(B) + \text{terms of higher order in } H\right] \cdot \tag{86}$$

Similarly one obtains, for the total number N_2 of electron-magnets in the "anti-parallel gas," a formula:

$$N_2 = L\left[\phi(B) + \frac{\mu_0 H}{kT}\phi'(B) + \text{terms of higher order in } H\right] \cdot \tag{87}$$

Now the total magnetic moment of the "parallel gas" is $N_1\mu_0$ in the same sense as the field, and the total magnetic moment of the "anti-parallel gas" is $N_2\mu_0$ in the sense opposed to the field; so that the net magnetic moment of the entire assemblage of electrons is $(N_1 - N_2)\mu_0$. We will carry out the computations only for values of H so low that we may ignore all terms beyond the second in the expansions for N_1 and N_2. The net magnetic moment is then approximately proportional to H; its quotient by H, the *susceptibility* χ of the electron-gas, is constant. It is a fact of experience that with nearly all paramagnetic substances the susceptibility *is* independent of H up to the highest attainable values of this variable. The limitation which we are here accepting will probably therefore not prove serious. Our approximative formula for χ is then as follows:

$$\chi = (N_1 - N_2)\mu_0/H = -\frac{2L\mu_0^2}{kT}\phi'(B) = -\frac{N\mu_0^2}{kT}\frac{\phi'(B)}{\phi(B)}, \qquad (88)$$

and all that remains is to make the step made in every previous case—to determine the last remaining unspecified constant, B, in terms of the total number N of the particles of the assemblage.

This number N is the sum of N_1 and N_2. Ignoring the terms of higher order in H, we have:

$$N = 2L\phi(B) \qquad (89)$$

and this is substantially the equation which was used to determine Sommerfeld's constant A in terms of N; for e^B and $1/A$ are one and the same. To make this equation identical with (63), or rather to make (63) identical with this one, we must there put $G = 2$, as we did—this is the reason for having introduced that factor G.

The procedure is then as follows: put $-B$ for log A in the right-hand member of equation (66)—differentiate it with respect to B—insert into the derivative the value of B obtained by equating to N the right-hand member of (66), *i.e.*, the value given in (67)—and substitute into (88). The resulting value for χ is this:

$$\chi = 12\left(\frac{\pi}{3}\right)^{2/3}\mu_0^2 n^{1/3} m_0 h^{-2}. \qquad (90)$$

To pass now to the experiments: is it permissible to suppose that the susceptibility of any metal is due entirely to the electron-gas within it? This is the same sort of uncertainty as confuses the question of the specific heat. Here we have every reason to expect that the magnetization of an ordinary paramagnetic metal is a threefold effect, involving not only the orientation of the electrons but also the orientation of the atoms, and finally that alteration of the electron-orbits in the atoms which gives rise to diamagnetism. To disentangle these three contributions to the net magnetic moment seems almost beyond the powers of any theory. With the alkali metals, however there is strong evidence that the second may be absent. Spectroscopic data show quite definitely that the magnetic moment of the alkali-metal ion—the atom minus its valence electron—is zero. If every atom in an alkali metal has surrendered its valence electron to the electron-gas, then there will be no orientation of the ions by the magnetic field, and the number of electrons forming the electron-gas will be equal to the number of atoms. The values of χ computed with this last assumption should then be not less than the actual susceptibility; they may be somewhat greater, because of the diamagnetic effect which is opposed in sign to the paramagnetic effect and therefore neutralizes it in part. Of this diamagnetic effect we can predict the order of magnitude, and we may expect that it will be greater, the higher the atomic number of the metal.

The value of χ proposed above is the value for absolute zero; for higher temperatures a closer approximation can be obtained by using two terms of the expansion in (66), instead of the first term only. It appears, however, that the alteration is slight. Like the average energy and the pressure, the susceptibility of the electron-gas should be very nearly the same at all temperatures from absolute zero up through room-temperature and far beyond. Now it is a fact that the susceptibility of the alkali-metals is independent of temperature—a fact so surprising, that the desire to explain it seems to have been Pauli's principal incentive in undertaking this research. For if the electron-gas were governed by the classical statistics, and the electrons were as many as the atoms, the susceptibility of a metal would increase as the temperature diminished and attain enormous values near the absolute zero.

When Pauli published the theory to which this section is devoted, the experimental data indicated that the susceptibilities of potassium and sodium were somewhat lower, those of rubidium and cæsium markedly lower than the predicted values—divergences which might be charged to the diamagnetic effect or to faults in the theory. Recent Canadian work, coming out very much *a propos*, has improved the situation remarkably. This tabulation (taken from E. S. Bieler, to whose article I refer for the sources) shows the comparison:

	Na	K	Rb	Cs
Theoretical (Pauli)	0.66	0.52	0.49	0.45
Experimental:				
McLennan et al.	0.61	0.42	0.31	0.42
Lane	0.65	0.54		

(All numerical values to be multiplied by 10^{-6})

Singularly enough, the agreements are too good! one would expect the diamagnetic effect to be more considerable than the very slight discrepancies between the experimental and the theoretical values for sodium, potassium, and cæsium. Perhaps further work on the theory of the diamagnetic effect would now be desirable.

Returning once more to the meaning of G, one sees that the placing of the value 2 for G in equation (61) and all of its descendants amounts to the making of the assumption that the electron-gas is really a mixture of two equally numerous and entirely independent assemblages of particles, each for itself obeying the Fermi statistics. This seems a rather odd idea, but inevitable.

Theory of Conduction

The new theory of conduction developed by Houston and Bloch is based upon the wave-theory of negative electricity, in which the interior of a metal is conceived to be filled not with darting corpuscles, but with stationary waves—as many distinct patterns of loops and nodes, it may be, as in the corpuscle-picture there are free electrons. It is not a consequence of the Fermi statistics alone, but of the Fermi statistics plus the wave-theory. Of course, if we come to decide that the Fermi statistics implies the wave-theory and *vice versa*, this warning will seem superfluous; but it is not superfluous, so long as the new statistics is used with reference to corpuscles. Now the corpuscle-picture of negative electricity is not only familiar, but seems likely to survive as the most convenient for describing most of the phenomena in which electrons figure. I will therefore express as much as possible of the new theory of conduction in the language of corpuscles, although eventually I shall be forced to make an assumption which will come to the same result as converting the corpuscles into waves.

To realize the things to be explained, conceive a slab of metal, having a thickness d measured along the x-axis; suppose a potential-difference V to exist between its faces, so that a field $E = V/d$ directed along the axis of x pervades it.

If the electrons in the metal moved perfectly freely, then any which was introduced without kinetic energy at the negative side of the slab would fall forthwith to the positive side, arriving there with the full kinetic energy eV and the full corresponding velocity of magnitude $(2eV/m)^{1/2}$ directed along the axis of x. Certainly nothing of the sort occurs. When a potential-gradient exists along a wire, for instance, heat is developed uniformly everywhere and there is nothing to suggest that the electrons are moving more rapidly at the positive than at the negative end.

We must then suppose that the free flight of the electron is interrupted at frequent intervals, and that at every interruption it loses the kinetic energy and the component of velocity up the potential gradient which it has acquired from the field since the last one previous. Or at least, the average loss of kinetic energy and of "drift-speed" at interruptions must be balanced by the average gain between interruptions.

In the corpuscle-theory these interruptions are pictured as actual impacts or collisions of the electrons with the atoms. Evidently, if we could assume that whenever an electron hits an atom it rebounds in some direction perfectly transverse to the field, then we should have a mechanism in which the drift-speed of the electron up the potential-gradient is annulled at every impact. This would be much too artificial. But if we think of both the electrons and the atoms as elastic spheres, the latter being so massive that they never budge when struck, the result is in effect the same. For then, the angle between the direction along which an electron approaches an atom and the direction along which it flies away after collision is *on the average* 90°. The rebound is as likely to be backward as forward; the rebounding sphere retains on the average no memory of its former direction of flight. This I will prove later.

There is a difficulty, which I must not leave unmentioned, although in this place I can do nothing to clear it away. In the development of these ideas we shall in effect assume that at the end of each free path the electron loses not only the forward drift-speed but the whole of the kinetic energy which it acquired while traversing that free path under the influence of the field. But if it collides with infinitely massive spheres it does not lose kinetic energy at all. If it collides with spheres of the mass of an atom, it loses kinetic energy, but does not completely lose its drift-speed. The theory of this latter case has been developed by Compton and Hertz for use in the study of conduction in gases, and might be applied to the problem presented by metals, but probably fits them no better than does the other hypothesis.

With this elastic-sphere model, then, the average interval between impacts is the average interval during which the electron is piling up drift-speed, only to lose it all at the end of the interval and be forced to start afresh from scratch. Denote by t_0 the length of this average interval. Since the acceleration of the electron is eE/m, its drift-speed at the end of the period t_0 is (eEt_0/m), its average drift-speed is half as great. Now I must dispel the impression that the drift-speed is the whole of the speed which the electron has. On the contrary, the mean speed of the thermal agitation—let me call it $\bar{v}$—is immensely larger than the small contribution which any ordinary field (indeed, any not very extraordinary field) can impart to an electron over a distance comparable with the distance between atoms. The field must not be supposed to do more than bend very slightly the rectilinear paths of the electrons from impact to impact. This statement is true with the classical statistics, *a fortiori* with the new. Denote by l the average distance traversed by an electron between impacts. Then t_0 is $l/\bar{v}$, and the average drift-speed is $\frac{1}{2}(eEl/m\bar{v})$.[13] The corresponding current-density is the product of this by the numer of electrons in unit volume multiplied by the charge of each. So, for the current-density produced by unit-field-strength, which is by definition the *conductivity* σ, we obtain the formula:

$$\sigma = \tfrac{1}{2}ne^2l/m\bar{v}. \tag{91}$$

The constant l, the *mean free path*, is the third disposable constant of the theory of electrons in metals.

I fear that the foregoing passage sounds very old-fashioned; but nevertheless it expresses the corpuscle-theory of conduction. The notion of elastic spheres is only accessory—an image which may or may not be the best to represent the central idea, the idea that the life-history of a corpuscle in a metal pervaded by a field is an alternation of gradual gain and sudden loss. The mean free path is the average distance of uninterrupted gain.

The common test of the formula (91) is the test by the temperature-variation. The result of this, incidentally, was regarded as quite as grave a demerit of the old electron-gas theory as the difficulty with the specific heat.

It is a fact of experience that the resistivity $\rho = 1/\sigma$ of any metal varies rapidly with temperature. For many metals it varies directly as T over quite a wide range; at low temperatures even more swiftly, not to speak of the strange phenomenon of supraconductivity. Now in equation (151) we have ρ set equal to a combination of two universal constants with three quantities $\bar{v}$, n, l between which last the responsibility for these great variations must be divided.

According to the classical statistics $\bar{v}$ is proportional to $T^{1/2}$. This is a variation in the right sense, but not fast enough. To make ρ vary as T we must then make nl vary as $1/T^{1/2}$. With the Fermi statistics the requirement is harder. The mean speed of thermal agitation is almost independent of temperature, and the burden of the whole responsibility for making ρ proportional to T must be loaded upon nl. The first step with the new statistics is a step backward.

Can we reasonably assume n to be the cause of the variation?

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[13] It is the mean of the reciprocal of the speed, not the reciprocal of the mean speed, which should figure here; but with so rough a formula the distinction is scarcely worth making.

If so, then it must diminish with rising temperature. It would seem reasonable enough for *n* to *increase* with rise of temperature, for presumably the free electrons arise from ionization of the atoms, and ionization is promoted by heat; but for *n* to *decrease* would seem very odd, notwithstanding Waterman's successes in accounting for some of the data by such a theory.

Part of the burden, then, must be cast on the mean free path—indeed the whole of it, if we adopt the new statistics so that $\bar{v}$ is held constant, and suppose in addition that *n* does not vary with temperature. But the elastic-sphere conception cannot stand the strain. It gives for the mean free path a value independent of temperature,[14] except insofar as the metal dilates with increase of heat. This is pretty nearly checkmate.

If however we might suppose that an electron may sometimes go clear through an atom without being reflected or deflected, and that the chance of such a piercing is relatively smaller and the chance of a rebounding relatively greater, the more violently the atom is vibrating—then by this theory the mean free path would diminish as the temperature rises, which is what is desired. This is an idea proposed long since by Wien.

The new idea is in result the same. The probability of the rebounding, or let me say of the *scattering* of an electron by an atom, is supposed to increase with the vigor of the vibrations of the latter. But for this a new reason is advanced: the reason, that while vibrating the atom is most of the time away from its equilibrium-place in the crystal lattice, and its relations with its companions are distorted. The probability of scattering is made to depend not only on the presence of the atom somewhere along the path down which the electron is rushing, but also on the relative positions of all the other atoms in the crystal.

To make such an assumption is, in effect, to compromise between the corpuscle-theory and the wave-theory. For what is the evidence from which it is inferred that a beam of light falling upon a grating, say, or a beam of X-rays falling upon a crystal, are undulatory? Essentially this: the way in which the beam is scattered or diffracted by the regular array of rulings on the grating or atom-groups in the crystal is different—greatly and strikingly different—from the way in which we know that it would be scattered by a single ruling, or suspect with good reason that it would be scattered by a single atom-

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[14] The value $1/N\pi R^2$ familiar in the kinetic theory of gases, N standing for the number of fixed spheres per unit volume, R for the sum of the radii of a fixed and a moving sphere.

group. For instance, there are directions in which no light at all is sent by the regular array, though assuredly light would be scattered in those directions by any member of the array if it were solitary. These facts are explained by invoking interference of waves. The wavelets expanding outwards from the various rulings or scattering particles are supposed to arrive in opposite phases at the "dark fringes" of the diffraction-pattern, so that they cancel each other. But one might also say that the beam of light is a stream of corpuscles which are deflected or scattered by the atom-groups or rulings which they happen to strike, and that the law of scattering of the individual atom-group is altered by the marshalling of the scattering elements into a regular pattern, so that in particular the probability of a deflection towards one of the dark fringes is reduced to zero.

I am not prepared to say that such a compromise is a full alternative for the wave-theory, though modern theoretical physics seems to be tending in that direction. But if we wish to describe with the language of the corpuscle-theory the phenomena of diffraction by a crystal, whether of waves of light or waves of negative electricity: then we must certainly adopt the idea of a probability-of-scattering, of a mean-free-path, which varies with the irregularity of the placing of the atoms.

The principle is especially simple and especially startling, if we deal with a beam of which the wave-length—considering it as a beam of waves—exceeds the spacing of the lattice. Waves of such a magnitude would not be diffracted at all by scattering particles placed exactly at the points of the lattice. Though any particle singly would scatter them, they flow through the lattice intact. If then we wish to interpret the beam as a stream of corpuscles, the probability of deflection of any corpuscle by any atom must sink to zero when the arrangement is made perfect; the mean free path must then be considered infinite.

The resistance of a perfect crystal of an element should then be zero when all the atoms are stationary in their places on the lattice—if they ever are, which apparently they are not; and should increase steadily with increasing temperature, in a way which can be computed if we know two things: the way in which the scattering of waves by particles on a lattice varies with the amplitude of the quiverings of the particles about their lattice-points, and the way in which the amplitudes of the particles vary with the temperature. The second of these questions is the subject of the theory of specific heats of solids, developed principally by Debye. The first has been profoundly studied by Debye and by several other physicists interested chiefly in the scattering of X-rays by crystals. Transferring their results into the theory of the diffraction of electron-waves, Houston demonstrated that over a wide range of temperatures the resistance of a perfect crystal should vary as the absolute temperature.

To determine not only the law of variation of resistance with temperature but the actual value of the resistivity for any metal, it would be necessary to evaluate the mean free path of the electrons. By the thoroughgoing corpuscular theory, this depends on the size of the atoms from which the corpuscles rebound; by the wave-theory, it depends on the scattering-power of the individual atom, which thus takes the place of the "size of the atom." The problem of computing the scattering-power of an atom for electron-waves belongs to the new mechanics. Houston was able to obtain good numerical agreements for several metals.

Another way of introducing irregularity into a crystal of an element consists in replacing a small fraction of the atoms, chosen at random here and there on the lattice, by atoms of another element. Certain alloys, known as "solid solutions," are of this type; and it is not only known that the resistance of such an alloy is greater than that of the element which is most abundant in it, but it has been shown by Nordheim that the dependence of resistance on percentage of substituted atoms follows the rule to be expected from the diffraction theory of resistance.[15]

Since then the conception of mean-free-path can be reinterpreted in terms of the wave-theory, and since it appears to be possible to deduce from the wave-theory a law of variation of mean-free-path with temperature which can be incorporated intact into the corpuscle-theory it is permissible to return to the corpuscle-picture to set up a theory of conduction of heat and of electricity, and of the thermo-electric effects in crystals.

We shall apply what I may call the method of the *perturbed distribution-function*, developed by Lorentz. The idea is, to begin by deriving a distribution suiting the actual case. The functions which we have hitherto employed, that of Maxwell and that of Fermi, are isotropic; it is only in the combination $(\xi^2 + \eta^2 + \zeta^2)$, hereafter to be called v^2, that the velocity-components ξ, η, ζ appear in them.[16] These "standard" functions may be appropriate to a uniform metal in which the temperature and the potential are uniform. Evidently they are not appropriate to a metal in which there is an electric field,

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[15] The idea that the free paths of electrons extend from one irregularity of the crystal to another was propounded before the advent of the wave-theory of negative electricity.

[16] I shall use the velocity-components hereafter in lieu of the momentum components, to conform with the custom.

or a temperature-gradient, or which varies in its chemical nature from place to place, as might an alloy. If in such a case we orient the axis of x parallel to the gradient of the variable quantity—be it electric potential, temperature, or whatever else—we must expect ξ to enter differently into the distribution-function from η and ξ.

Various arguments show that as a rule the departures from the standard function must be rather small. Lorentz therefore postulated that in the presence of a gradient directed parallel to the x-axis, the actual distribution should differ from the standard function $f_0(v)$ —this he of course assumed to be Maxwell's—by virtue of a small additive term, a new function of v multiplied by the velocity-component ξ:

$$f = f_0(v) + \xi g(v), \tag{92}$$

and he proceeded to determine the new function g by the condition that f should remain constant in time despite the collisions of the electrons with the atoms. More precisely, he found for each of the three cases with which we shall be concerned a function g, such that the distribution-function obtained by adding ξg to f_0 conforms to that condition. This justifies the procedure.

Much the simplest case of the three is that of a uniform metal at a uniform temperature, subject to an electric field; for here the distribution-function need not vary from place to place. It will be well to go through the reasoning in this instance, though the formula for conductivity in which it leads differs but little from (91).

It is required, to find a function g of the combination $(\xi^2 + \eta^2 + \zeta^2)^{1/2}$ such that if at any moment the distribution $(f_0 + \xi g)$ prevails, it continues unchanged throughout time—the number of particles in any compartment or cell of the velocity-space (the momentum-space of the earlier pages, with its unit of length altered in the ratio $m : 1$) stays constant. Choose a compartment enclosed between planes ξ and $\xi + d\xi$, η and $\eta + d\eta$, ζ and $\zeta + d\zeta$. Call it the compartment C. Its volume is $d\xi d\eta d\zeta$, which to save a profusion of Greek letters I will usually denote by $d\tau$. The number of particles in it is $f \cdot d\tau$. This number must remain unchanged, though individual particles are constantly moving into and out of C in either of two ways—by "drift" and by "collision."

Owing to the field E, all of the particles have a steady acceleration $\alpha = eE/m$, because of which they are continually and continuously drifting from cell to cell. One easily sees that the number which thus drift out of C per unit time (it is best to think of "unit time" not as one second, but as a period small compared with the mean time between impacts) is equal to first approximation to $\alpha f(\xi + d\xi, \eta, \zeta) d\eta d\zeta$.[17] This loss is partly balanced by an inward drift of particles which are accelerated into the compartment from the one lying beyond the plane ξ; the balance is not perfect, for the number drifting in per unit time is equal to $\alpha f(\xi, \eta, \zeta) d\eta d\xi$ and there is a difference $\alpha(df/d\xi)d\tau$ outstanding.[18] This difference must be balanced by the entrances and exits of particles which undergo collisions.

Let adt represent the number of electrons which, being initially in the compartment C, suffer impacts during unit time and are thus suddenly bumped out of it; and bdt the number which, being initially in other compartments, suffer such impacts during unit time that they suddenly turn up in C. The function g must be so chosen, that the lack of balance between the electrons drifting out and the electrons drifting in is just compensated by the lack of balance between those bumped into the compartment and those which are bumped out:

$$\frac{eE}{m}\frac{df}{d\xi} = b - a. \tag{93}$$

We must therefore evaluate $(b - a)$ in terms of the distribution-function.

We already have a formula ready-made for the number of impacts experienced per unit time by the particles of speed v; it is v/l for each particle, so that:

$$a = (v/l) f d\xi d\eta d\zeta. \tag{94}$$

Since however we have also to compute b, we shall find it expedient to classify these impacts according to the destinations of the particles, so to speak—according to the compartments of velocity-space into which they are bounced. A particle of speed v is located, in the velocity-space, on a sphere of radius v centered at the origin. Collision with an immovable atom changes the direction, but not the magnitude of the velocity; in the velocity-space, the particle suddenly moves to some other point on the same sphere. When electrons jump out of the compartment C because of impacts, they land in the other compartments which with C form a spherical layer around the origin. When electrons jump into C because of impacts, they come from the other compartments of that same layer. We shall derive an expression

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[17] During a time dt so short that αdt is small by comparison with $d\xi$, the particles which initially lie between the plane $(\xi + d\xi - \alpha dt)$ and the side $(\xi + d\xi)$ of the compartment move out of it, while the particles which initially lie between the side ξ of the compartment and the plane $(\xi - \alpha dt)$ move into it; these two classes of particles number $f(\xi + d\xi, \eta, \zeta)\alpha dt \cdot d\eta d\zeta$ and $f(\xi, \eta, \zeta)\alpha dt \cdot d\eta d\zeta$ respectively.

[18] This expression figures in the equations as a net loss, but in fact has a negative sign (since $df/d\xi < 0$) and therefore is actually a gain.

for the number of particles leaping from C into any other cell C' of the layer, and an expression for the number leaping reversely. The difference or lack of balance between these numbers, integrated over all the cells C', will be the required quantity $(b - a)$.

We begin by inquiring how many particles make such impacts that their paths (in the coordinate-space, of course—not the velocity-space) are deflected through angles between say θ and $\theta + d\theta$. To be deflected through an angle θ, an electron must strike an atom at a point where its surface is so oriented, that the normal (which is the line of centres at the instant of collision) is inclined to the line of approach of the electron at the angle $\psi = \frac{1}{2}(\pi - \theta)$. Denote by R the radius of the atom, and suppose that the radius of the electron is negligibly small.[19] Think of all the $f \cdot d\xi d\eta d\zeta$ electrons which at some particular moment of time are in unit volume of the metal, and belong to the compartment C of the velocity-space. Imagine each of these to be the centre, in the coordinate-space, of a pair of circles lying in the plane perpendicular to its path, and having radii $R \sin \psi$ and $R(\sin \psi + d \sin \psi) = R(\sin \psi + \cos \psi d\psi)$. As time goes on, let these circles travel in the direction normal to their plane with the speed v. During unit time each pair of circles traces out a pair of cylinders of length v, containing between them a cylindrical sheath of volume $v \cdot 2\pi R^2 \sin \psi \cos \psi d\psi$. Multiplying this by the number $f \cdot d\xi d\eta d\zeta$ of the electrons, we get the total volume included in all of these sheaths. Multiplying this by the number N of atoms in unit volume, we get the number of atoms located with their centres in these sheaths—which is the number of atoms so placed that in unit time, electrons of the stated cell impinge on them at angles between ψ and $\psi + d\psi$—which is the number of impacts per unit time in which electrons are deflected through angles between θ and $\theta + d\theta$, which accordingly is this:

$$N \cdot f d\xi d\eta d\zeta \cdot 2\pi v R^2 \sin \psi \cos \psi d\psi = f d\xi d\eta d\zeta \cdot N\pi R^2 v \cdot \tfrac{1}{2} \sin \theta d\theta. \quad (95)$$

It will be convenient to express this as a fraction of the total number of impacts—call it $Z d\tau$—experienced per unit time by all the electrons in question, which by integrating (95) is found to be:

$$Z d\tau = \pi N R^2 v \cdot f \cdot d\tau, \quad (96)$$

substituting which into (95) we get:

$$Z \cdot 2 \sin \psi \cos \psi d\psi = Z \cdot \tfrac{1}{2} \sin \theta d\theta. \quad (97)$$

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[19] The formulæ remain valid even if the diameter of the electron is supposed not negligibly small, provided that we interpret R as the sum of the radii of atom and electron; but the generalization is not, so far as I know, of any practical value.

It will be observed that deflections smaller than 90° are equally numerous with deflections greater than 90°, so that on the average the electrons after impact have no reminiscence of their prior direction of motion, as I mentioned earlier. Also, comparing (96) with (94), one derives the expression for mean free path,

$$l = 1/N\pi R^2, \tag{98}$$

cited already in a footnote. To appreciate the most important feature of the expression (97) we must however return to the velocity-space.

In the velocity-space, the electrons of which the paths in coordinate-space are deflected through angles between 2θ and $2\theta + d2\theta$ execute leaps from the compartment C into other compartments of the spherical layer aforesaid, located on a certain region thereof. These occupy a belt or collar on the sphere, intercepted between two cones drawn with their common apex at the centre, their common axis pointing towards C and their apical semi-angles equal to θ and $\theta + d\theta$ respectively. Now the area of this belt is itself proportional to $\sin \theta d\theta$. This is very important: for it means that the electrons which are bounced out of C by collisions are sprinkled uniformly over all the rest of the sphere. More yet: it means that the electrons which are bounced out of *any* cell of the spherical layer are sprinkled uniformly through all the rest of the layer.

Consider then the interchange of electrons between two cells of the layer, say C at (ξ, η, ζ) with volume $d\tau$, and C' at (ξ', η', ζ') with volume $d\tau'$. The number leaping from C to C' is equal to the total number of impacts occurring in C multiplied by the ratio which the volume of C' bears to the volume V of the layer. The number leaping from C' to C is equal to the total number of impacts occurring in C', multiplied by the ratio which the volume of C bears to the volume of the layer. The excess of the latter over the former is then:

$$Z(\xi', \eta', \zeta')d\tau'(d\tau/V) - Z(\xi, \eta, \zeta)d\tau(d\tau'/V), \tag{99}$$

which with the aid of (96) and (98) may be written thus:

$$\frac{vd\tau}{l}[f(\xi', \eta', \zeta') - f(\xi, \eta, \zeta)]d\tau'. \tag{100}$$

This is the quantity of which the integral with respect to ξ', η', ζ', extended over the spherical layer, is equal to $(b - a)d\tau$—the net rate at which compartment C gains particles through impacts.

Making Lorentz' postulate about the form of the distribution-function f, and remembering that throughout the spherical layer the combination $(\xi'^2 + \eta'^2 + \zeta'^2)^{1/2}$ is confined within a narrow range of values around v we obtain:

$$b - a = (v/l)\cdot\mathfrak{g}(v)\cdot\int(\xi' - \xi)d\tau'/V. \tag{101}$$

To effect the integration it is expedient to change over to polar coordinates in the velocity-space. Leaving the origin where it was, and directing the polar axis towards C, we make the radial coordinates and the colatitude-angle identical with our v and θ, and for the meridian-angle we use the symbol ϕ. Dividing up the layer into compartments by latitude circles and meridians, we have for any one of them:

$$d\tau'/V = (1/4\pi)\sin\theta d\theta d\phi. \tag{102}$$

Consequently we obtain:[20]

$$b - a = (v/4\pi l)g(v)\cdot\int_0^\pi d\theta\sin\theta\int_0^{2\pi}d\phi(\xi' - \xi). \tag{103}$$

Everything therefore hinges on the evaluation of $(\xi' - \xi)$—the change in the x-component of velocity which the electron incurs when it leaps from C' to C—as a function of θ and ϕ. Now it may be shown without much difficulty,[21] that:

$$\xi' - \xi = -2v\cos\psi\cos\omega = -2v\sin\tfrac{1}{2}\theta\cos\omega \tag{104}$$

wherein ψ stands as before for the angle between the line of approach of the electron and the line of centres at the instant of impact, and ω stands for the angle between the line of centres and the axis of x. There is also a standard formula[22] relating $\cos\omega$ to ψ, ϕ and the

[20] Lest someone be disconcerted by the apparent difference between this equation and that given by Lorentz, I remark that I am using θ to designate an angle twice as great as the one which he denoted by θ.

[21] Let $\boldsymbol{v}$, $\boldsymbol{v}'$ represent the vector velocities of the electron before and after impact, $\boldsymbol{c}_1$ the unit vector along the line of centres at the moment of impact. The components of $\boldsymbol{v}$ and $\boldsymbol{v}'$ along the line of centres are equal in magnitude and opposite in direction; the components perpendicular to the line of centres are equal in magnitude and direction. Writing these statements down in vector notation:

$$\boldsymbol{v}\cdot\boldsymbol{c}_1 = \boldsymbol{v}'\cdot\boldsymbol{c}_1;\ \boldsymbol{v} - (\boldsymbol{v}\cdot\boldsymbol{c}_1)\boldsymbol{c}_1 = \boldsymbol{v}' - (\boldsymbol{v}'\cdot\boldsymbol{c}_1)\boldsymbol{c}_1 = \boldsymbol{v}' + (\boldsymbol{v}\cdot\boldsymbol{c}_1)\boldsymbol{c}_1, \text{ hence,}$$
$$\boldsymbol{v}' - \boldsymbol{v} = -2(\boldsymbol{v}\cdot\boldsymbol{c}_1)\boldsymbol{c}_1 = -2v\cos\psi\cdot\boldsymbol{c}_1;\ \xi' - \xi = -2v\cos\psi\cos\omega.$$

[22] Imagine two planes P_1 and P_2 intersecting along a vertical axis, the dihedral angle between them being ϕ. Through a point O on the axis draw a horizontal plane N, and from O draw two lines of unit length OR_1 and OR_2, the former in plane P_1 and inclined at β to the vertical axis, the latter in plane P_2 and inclined at ψ to the vertical axis; ω is the angle between them. The points R_1 and R_2 are at heights $\cos\beta$ and $\cos\psi$ above the plane H. On the vertical line through R_2 put a point R_3 at distance $\cos\beta$ above H. Expressions for the sides of the right-angled triangle $R_1R_2R_3$ are easily obtained, and (214) is derived by applying the theorem of Pythagoras to them.

angle $\beta = \text{arc cos } (\xi/v)$ between the initial path of the electron and the axis of x, as follows:

$$\cos \omega = \cos \beta \cos \psi + \sin \beta \sin \psi \cos \phi. \tag{105}$$

We now have everything necessary to do the integration in equation (103), and we find:

$$b - a = (v\xi/l)g(v). \tag{106}$$

Substituting this into equation (93), the condition that the distribution-function $(f_0 + \xi g)$ shall be stable by virtue of perfect balance between the rates at which electrons are shifted from compartment to compartment by the impacts and by the accelerating field, we get:

$$(eE/m)\frac{d}{d\xi}(f_0 + \xi g) = (v\xi/l)g. \tag{107}$$

If the term $\xi g(v)$ is truly small by comparison with the term $f_0(v)$, we may neglect the second term on the left; and since $(df_0/dv) = (df_0/dv)(dv/d\xi) = (\xi/v)(df_0/dv)$, the culmination of all the argument is in the formula:

$$\xi g(v) = \frac{\xi l}{v^2}\frac{eE}{m}\frac{df_0}{dv} \tag{108}$$

for the alteration which the applied electric field imposes on the distribution. Notice that g involves ξ and η and ζ only in the combination v; this justifies the procedure of Lorentz.

Now each electron which during unit time crosses any surface imagined in the metal contributes an amount e to the current through that surface; but the contributions made by electrons crossing in opposite senses are opposite in sign—what we perceive as current is *net* current, the excess of the flow of charge one way over the flow the other. Conceive a plane surface-element of area da, normal to the field, therefore normal to the axis of x. We must classify the electrons which traverse it according to their values of ξ. Let $H(\xi)d\xi da$ represent the number passing through in unit time, and having at the moment of passage x-components of velocity in the range $d\xi$ at ξ. This is equal to the number which at any instant have their x-components of velocity in this range, and are situated in the right prism having da for its base and extending a distance ξ down the direction of x:[23]

$$H(\xi)d\xi da = \xi da d\xi \int_{-\infty}^{\infty} d\eta \int_{-\infty}^{\infty} d\zeta f(\xi, \eta, \zeta). \tag{109}$$

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[23] This would be immediately obvious, if all the electrons were moving parallel to the x-axis and made no impacts. Electrons having y and z components of velocity in addition to the x-component will drift obliquely out of the prism, and electrons making impacts will be thrown out of the range $d\xi$; but each electron thus lost will be balanced by another coming in from outside.

Since for electrons crossing in opposite senses ξ is of opposite signs, the integral of this expression over all values of ξ, multiplied by e, gives the net current through da when the proper distribution-function is inserted. Evidently the integral will vanish when f is isotropic; there are enormous flows of charge both ways through da, but they are balanced. Unbalance is brought about by the non-isotropic perturbation-term in the distribution-function. Making the postulate of Lorentz, we obtain for the net current through unit area perpendicular to the field, the current-density J, the expression:

$$J = e\int H(\xi)d\xi = e\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\xi d\eta d\zeta \cdot \xi^2 g(v). \tag{110}$$

Set for $g(v)$ the expression in (217), and to effect the integration transform into polar coordinates in the velocity-space, orienting the polar axis along the axis of ξ; integrating over the angles, one obtains:

$$J = \frac{le^2E}{m}\frac{4\pi}{3}\int_0^\infty v^2 \frac{df_0}{dv}\,dv. \tag{111}$$

The final integration is easy if one chooses for f_0 the Maxwell function, not quite so easy if one chooses that of Fermi. A further step will be of some advantage. Integrating by parts, and noticing that v vanishes at the lower and f_0 at the upper limit, we find:

$$J = -\,(8\pi le^2E/3m)\int_0^\infty f_0 v dv \tag{112}$$

and the integral remaining, divided by n the number of electrons per unit volume, is seen to be $1/4\pi$ times the mean value of v^{-1},—the average of the reciprocal of the speed of the electrons, in the absence of the field. Denoting this by $\overline{v^{-1}}$, we may write as the general formula for conductivity:

$$\sigma = \frac{J}{E} = \frac{2}{3}\frac{le^2n}{m}\overline{v^{-1}}. \tag{113}$$

The analogy with (91) is obvious, but we must not be misled into identifying the average of the reciprocal speed with the reciprocal of the average speed; they are not quite equal.

The actual final formulæ obtained by the old and the new statistics —substituting, that is to say, the appropriate values of $\overline{v^{-1}}$ from (72b) and (72a), and putting $G = 2$—are as follows:

$$\sigma = \frac{4}{3}\frac{e^2ln}{(2\pi mkT)^{1/2}} \quad \text{(old)}, \tag{114a}$$

$$\sigma = \frac{8\pi}{3}\frac{e^2l}{h}\left(\frac{3n}{8\pi}\right)^{2/3} \quad \text{(new)}. \tag{114b}$$

As Sommerfeld has shown, all of the reasoning by which (108) was reached remains intact even when it is supposed that l is a function of v; in that case, l remains under the integral sign in (111), and the integral itself is equal to $n/4\pi$ times the mean value of $v^{-2}d(lv^2)/dv$. This generalization may be of some value.

Uniform Metal with a Temperature-Gradient; Thermal Conduction

We have now to find a function g such that the distribution $(f_0 + \xi g)$ is stable in a metal in which there is a constant gradient of temperature along the axis of x. When we find it, we shall be able to evaluate the integral

$$W = \tfrac{1}{2}m \int\int\int d\xi d\eta d\zeta \cdot g(v)v^2\xi^2, \tag{115}$$

which is like the integral in (219) except for the differently-chosen form of g and the substitution of $\frac{1}{2}mv^2$ for e, and therefore represents the net rate of flow of kinetic energy borne by electrons through unit area perpendicular to the gradient—the contribution of the electrons to the flow of heat, under the circumstances stated.

The standard distribution-function f_0, involving as it does the temperature T, is in this case itself a function of x. One might expect that this dependence of f_0 on x would be sufficient to fulfil the requirements. An isotropic distribution which varies from point to point cannot however be stable; the particles conforming to such a one at any given moment would proceed to drift off down the gradient. A stable distribution cannot be isotropic. We must repeat the process of balancing the rates at which particles enter and leave each compartment of the phase-space through collisions and through drift. I say the phase-space now, instead of the velocity-space; for this case is made more complicated than the previous one by reason of the fact, that we now must make the balance separately for the electrons contained in each of the six-dimensional cells $d\xi d\eta d\zeta dxdydz$, whereas previously we could make it *en bloc* for all of the particles in the entire metal comprised within any velocity-cell $d\xi d\eta d\zeta$.

Consider then the six-dimensional cell $d\xi d\eta d\zeta dxdydz = ds$, and the $f(\xi, \eta, \zeta, x, y, z)ds$ electrons in it. The first three factors in ds denote the range of velocity, the last three the range in position, within which an electron must lie if it is to belong to ds. Electrons in the proper range of position are continually entering or leaving the proper range of velocity, because of impacts. The net rate at which ds gains electrons in this way is given, as before, by (106). Electrons in the proper range of velocity are continually drifting into the proper range of position, coming into $dxdydz$ from the region adjacent to it on the side towards smaller or greater values of x, according as ξ is positive or negative. By the same sort of reasoning as led to the term $\alpha df/d\xi$ in (93), one sees that the net rate at which ds loses electrons in this way is $\xi df/dx$. Equating the two, we have:

$$\xi df/dx = b - a = (\xi v/l)g(v), \tag{116}$$

and when we put f_0 for f as before, on the ground that the term (ξg) in the full expression for f makes but a small contribution to the left-hand member, we have all that is required for computing g from (116) and W from (115) for whatever standard function we elect.

At this point, however, there arises a difficulty. If having adopted this way of determining g we proceed to compute the electric current J in the metal by formula (110) we find that it is not zero. The reasoning has led to the conclusion that wherever there is a net current of heat in a metal, there is also a net current of electricity. This conclusion is not in accord with experiment. Yet there is apparently no other way to circumvent it, than to suppose that when a gradient of temperature is maintained in a metal there arises a spontaneous internal electric field, of just such a magnitude as to counteract the electric current which would otherwise persist. The gradient of temperature calls forth a gradient of potential; the actual distribution-function is the one which is stable under both these gradients combined. In the bookkeeping of the compartment ds, the net gain from impacts $(b - a)$ is balanced against the sum of the net loss through drift in the coordinate-space $(\xi df/dx)$ and the net loss through drift in the velocity-space $(\alpha df/d\xi)$. Putting these statements into the form of equations, and denoting by E the hypothetical electric field and by $\alpha(= eE/m)$ the acceleration which it imparts to each electron, we have:

$$\alpha(df/d\xi) + \xi(df/dx) = b - a = (\xi v/l)g \tag{117}$$

$$J/e = \int\int\int d\xi d\eta d\zeta \cdot \xi^2 g = 0, \tag{118}$$

a pair of equations for determining E and the function g.

Lorentz, adopting the Maxwell-Boltzmann function for f_0, solved the equations, and obtained:

$$W = \frac{8}{3}\frac{nlk^2T}{(2\pi mkT)^{1/2}}\left(\frac{dT}{dx}\right) \qquad \alpha = \frac{1}{2}\frac{k}{m}\frac{dT}{dx}. \tag{119}$$

Sommerfeld adopted the Fermi function, and obtained for the degenerate case:[24]

$$W = \frac{8\pi^3}{9}\frac{lk^2T}{h}\left(\frac{3n}{8\pi}\right)^{2/3}\left(\frac{dT}{dx}\right). \tag{120}$$

The coefficient of dT/dx in these expressions for W is by definition the *thermal conductivity*, usually denoted by κ. One notices that these expressions for κ like those for σ, involve the more or less disposable constants n and l. This however is not true of the ratio of the conductivities.

The Wiedemann-Franz Ratio

For the ratio of thermal to electric conductivity, the old statistics and the new supply expressions involving nothing but T and the ratio of the universal constants k and e, and differing only by a slight numerical factor:

$$\kappa/\sigma = 2(k/e)^2T(= 4.2 \times 10^{-11} \text{ at } T = 291° K) \tag{121}$$

by the old statistics, and

$$\kappa/\sigma = \tfrac{1}{3}\pi^2(k/e)^2T(= 7.1 \times 10^{-11} \text{ at } T = 291° K) \tag{122}$$

by the new.

This "Wiedemann-Franz ratio" seems to have been predestined to encourage the devotees of the electron-gas theory. Every other formula offered by the theory contained either n or l or both, and therefore could not serve as an ultimate critical test; for any discrepancy with the data could be removed by adjusting these constants. True, the ensemble of the formulæ provided by the classical theory ran counter to the data in so many different ways, that the net result was quite unfavourable; but one could not point out any single prediction which was certainly wrong. If however the Wiedemann-Franz ratio had departed by an order of magnitude or more from the value of $2(k/e)^2T$, the electron-gas theory could hardly have survived the blow. But in this one case where disagreement would have been fatal, there was agreement; not perfect, but rather too good to be discarded as fortuitous. For many of the familiar metals the ratio, when measured at room-temperature, turned out to be around 6 or $7 \cdot 10^{-11}$. This more than any other one fact was what kept alive the feeling, that in spite of all its difficulties the electron-gas theory must be fundamentally right.

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[24] To derive this formula it was necessary to proceed to the second-approximation expression for the Fermi distribution-function; the first approximation merely yielded zero for W.

For the twelve metals Al, Cu, Ag, Au, Ni, Zn, Cd, Pb, Sn, Pt, Pd and Fe, the average of the values of κ/σ at 291° K is $7.11 \cdot 10^{-11}$. The agreement with the prediction of the new statistics is more than good. It is so very good, that it must be partly accidental, especially as the individual values from which the average is formed depart from it by varying amounts. One may still doubt whether it is to be admitted as one of the items which compel the adoption of the new statistics. Drude, be it recalled, obtained the value $6.3 \cdot 10^{-11}$ out of the crude assumption that all of the electrons in any volume-element have the same speed.[25] It used to be regarded as rather amusing that the elaborate calculations of Lorentz merely impaired the agreement which Drude had attained in a naively simple way.

Both theories require that the ratio be proportional to T; this is fairly well satisfied over wide ranges of temperature, but at extreme degrees of cold there is marked divergence, which is inconvenient. It may be desirable to invoke other mechanisms of conduction to supplement the free electrons—as for instance the passing-along of electrons from atom directly to atom to assist in the conduction of electricity, or the transmission of elastic vibrations to aid in the transfer of heat. Indeed, when one reflects that insulators though they lack free electrons yet have some device for the transmission of heat, one wonders why this device should not be available to metals also, and exalt their values of κ and of κ/σ above the predictions of the electron-gas theory.

Intrinsic Potential Difference

We have seen that in a metal where there is no electric current and yet there is a current of heat, an internal electric field must be imagined. We shall now see that in a metal where there is no electric current, but the number of electrons per unit volume varies from point to point, there must also be an internal electric field. This sounds plausible to intuition, for one would expect the electrons to diffuse from regions of higher to regions of lower density unless they were impeded by some force. The equations (117) and (118) enable us to evaluate this force.

Returning to these equations, introduce polar coordinates v, θ, ϕ in the velocity-space as we have formerly done; then $\xi = v \cos \theta$. Multiply both sides of equation (117) by $\cos \theta$; the right-hand member of the new equation is then proportional to $\xi^2 g$. Integrate both

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[25] Drude of course could evaluate the ratio k/e without knowing either k or e accurately or at all, since it is the same as the ratio N_0k/N_0e — N_0 standing for the number of molecules in a gramme-molecule, the Loschmidt number—and N_0k is the gas-constant R while N_0e is the Faraday constant of electrolysis.

members of this new equation over the entire velocity-space. The integral on the right then vanishes by reason of (118), and for the integrals on the left we have:

$$\alpha \int d\tau (df_0/d\xi) \cos \theta + \int d\tau \xi (df_0/dx) \cos \theta = 0. \tag{123}$$

By obvious transformations we get:

$$\alpha \int d\tau \frac{df_0}{dv} \cos^2 \theta + \frac{d}{dx} \int d\tau f_0 v \cos^2 \theta = 0. \tag{124}$$

Integrating over the angles:

$$\frac{4\pi}{3} \alpha \int \frac{df_0}{dv} v^2 dv^3 + \frac{4\pi}{3} \frac{d}{dx} \int f_0 v^3 dv = 0. \tag{125}$$

Leaving the second term as it is, but integrating the first by parts, we find that as f_0 vanishes (whichever statistics we use) at one limit and v at the other limit of integration, we get:

$$-\frac{2}{3} \alpha \int 4\pi f_0 v^{-1} \cdot v^2 dv + \frac{1}{3} \frac{d}{dx} \int 4\pi f_0 v \cdot v^2 dv = 0. \tag{126}$$

The integrals are written in this curious fashion, to bring out the feature that they are proportional to the mean values of functions—the functions v^{-1} and v, respectively—averaged over the electrons in question; which is to say, all the electrons contained in the compartment $dxdydz$ of coordinate-space, to which equation (117) has reference. They are in fact equal to the products of these mean values, to wit the *mean reciprocal speed* and the *mean speed*, by the number $ndxdydz$ of the electrons in the compartment $dxdydz$. Rewriting (125) accordingly, with overlinings to signify averages, and dividing out the factors $dxdydz$ and 1/3, we get:

$$-2\alpha n\overline{v^{-1}} + d(n\bar{v})/dx = 0, \tag{127}$$

and this is the equation for the acceleration α or the accelerating field $E = m\alpha/e$, required to counteract the electric current which otherwise would be produced in the presence of the gradient $d(n\bar{v})/dx$ of the quantity $n\bar{v}$. This is the gradient which evokes the hypothetical electric field; gradients of temperature or of concentration act indirectly, by making $n\bar{v}$ vary.

With the classical statistics the development is extremely simple, for $\bar{v}$ depends on temperature only, while n may be varied at will.

Heretofore we have tacitly assumed that n remains the same while T and therefore $\bar{v}$ vary along the axis of x, so that:

$$d(n\bar{v})/dx = nd\bar{v}/dx = n(d\bar{v}/dT)(dT/dx), \tag{128}$$

and the reader can verify the expressions for α and W given in (119) by starting from this point. But now we will assume that T and $\bar{v}$ remain the same while n varies along the x-direction with a gradient dn/dx. Then:

$$d(n\bar{v})/dx = \bar{v}\cdot dn/dx. \tag{129}$$

Putting this into (127), and recalling that in the Maxwell distribution the mean values of v and v^{-1} are thus related,

$$\bar{v} = (2kT/m)\overline{v^{-1}}, \tag{130}$$

one perceives that $\bar{v}$ disappears by division from the two sides of the equation, leaving this:

$$\alpha n = (eE/m)n = (kT/m)dn/dx, \tag{131}$$

the desired equation for the necessary electric field. Integrating it, we obtain another of very familiar aspect:

$$n = n_0 \exp{(eE/kT)(x - x_0)} = n_0 \exp{(-[V - V_0]/kT)}. \tag{132}$$

This is the celebrated equation of Boltzmann embodying the statement that if in an assemblage of particles at uniform temperature there are variations in the number-per-unit-volume from place to place, then there must also be a field of force against which work must be done to move a particle from place to place—and *vice versa*. Specifically: if at any two points P and O the number-per-unit-volume of the particles has values n and n_0, there must be a field of force such that when a particle is moved from O to P its potential energy is increased by $- kT\cdot log(n/n_0)$. If the particles are electrons and the field of force is electric and derived from a potential having values V at P and V_0 at O, then of course this change in potential energy is expressed by $e(V - V_0)$.

Boltzmann's equation is so deeply rooted in modern physics, that it seems strange and suspicious that the new statistics should substitute another but it does. The reason for the innovation stands out very clearly in (127) when the absolute-zero extreme of the Fermi distribution is applied. Owing to the dependence of $\bar{v}$ on n, *owing to the interrelation between average speed and number per-unit-volume* which distinguishes a system conforming to the new statistics, the second term in (127) is no longer proportional to dn/dx. Instead, we have:

$$n\bar{v} = \frac{3}{4}nv_m = \frac{3hn}{4m}\left(\frac{3n}{4\pi G}\right)^{2/3}; \qquad \overline{v^{-1}} = 3/2v_m, \tag{133}$$

substituting which values into (237), we obtain:

$$eE/m = \alpha = \frac{h^2}{3m^2}\left(\frac{3}{4\pi G}\right)^{2/3} n^{-1/3}dn/dx, \tag{134}$$

and integrating:

$$-E(x - x_0) = +(V - V_0) = \frac{h^2}{2me}\left[\left(\frac{3n}{4\pi G}\right)^{2/3} - \left(\frac{3n_0}{4\pi G}\right)^{2/3}\right]. \tag{135}$$

This is the formula which supplants Boltzmann's equation.

Consulting (71), we see that (135) may be rewritten thus:

$$e(V_1 - V_0) = (W_i)_1 - (W_i)_0, \tag{136}$$

which is to say: if there is equilibrium between two samples of electron-gas, both being at absolute zero and distributed according to the Fermi law, and the fastest electrons of the two having values of kinetic energy W_{i1} and W_{i0} respectively—then there is a potential-difference between the two, such that if the fastest electron of either group were to cross over to the other, its kinetic energy on arrival would be equal to that of the fastest electron of the group which it joins. So stated, the proposition is easy to remember, and one might even come to think it obvious.

Consider now a pair of pieces of different metals, in contact with one another. One may conceive that they are welded together by an alloy in which the proportion of either varies continuously from zero to one hundred per cent, if one feels the need for a mathematical continuity. If the two pieces were separate, the number of electrons per unit volume would probably not be the same for the two; certainly it is not the same if the number of electrons is equal to the number of atoms per unit volume, for this varies from metal to metal. If the process of welding the metals together does not alter the concentration of the electrons in either at points remote from the junction, then a potential-difference given by (132) or (135)—according as the old or the new statistics is the proper one—must arise between the metals. Taking Sommerfeld's example of potassium and silver: if in unit volume of each of these metals there are as many electrons as atoms, and if this state of affairs continued when the two are welded together, then between the interiors of the metals across the weld there must be a potential-difference of 4.2 volts,[26] potassium being negative. This figure is calculated by the formula (135); the classical formula gives a value considerably lower, about 0.04 volt. This contrast is characteristic. Both the new and the old statistics associate an internal or intrinsic potential-difference with a difference in electron-concentration, and *vice versa;* but the amount of the P. D. associated with a given pair of concentrations is by no means the same by the two theories; and in actual cases, the new statistics gives much the larger amount.

Though it is not actually possible to measure the potential in the interior of a metal, there are phenomena which indicate that between two metals touching one another, or between two parts of a metal maintained at different temperatures, there is a difference of potential. These are the *thermoelectric* phenomena—Peltier effect, Thomson effect, thermal electromotive force. The internal potential-gradient reveals itself through the fact that when an electric current is sent through the region where it exists, the rate of generation of heat departs from that which is calculated by Joule's law. We must therefore apply the statistics—this will be the last application which I shall consider—to the problem of evaluating the transport and the generation of heat in an electron-gas, in which the distribution-function is perturbed by an electric field and simultaneously by either of the two other influences—varying temperature, varying concentration of electrons—which we have heretofore considered separately.

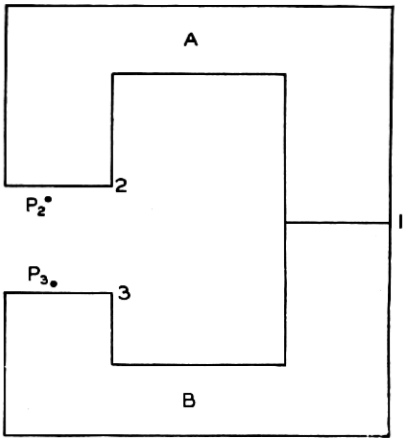

Fig. 2.

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[26] Sommerfeld originally computed 5.7 volts, having put $G = 1$; the value 4.2 corresponds to $G = 2$.

Before undertaking this I had better dispel any notion that the "contact" or "Volta" potential-difference between a pair of metals is the measure of the P. D. between their interiors for which we have just been deriving theoretical expressions. It is in fact a measure of something else, as one sees by examining an arrangement like that of Figure 2, where A and B signify pieces of two metals which are in contact at 1, and face one another across a gap between 2 and 3. Consider an electron anywhere inside A, and estimate the potential-barriers which it must cross in order to arrive at the point P_2 just outside of the boundary 2, and also those which it must cross in order to pass through the metal B and reach the point P_3 just outside of the boundary 3. Recalling the symbols and the relations introduced in the section on thermionics, one sees that there is a potential-difference between P_2 and P_3 given by the expression

$$(W_{aA} - W_{aB}) - (W_{iA} - W_{iB}) = b_A - b_B. \tag{137}$$

This is the contact potential difference; and we see that if the new statistics is correct, it is equal (at the absolute-zero limit) to the difference between the values, for the two metals in question, of that quantity b which appears in Richardson's equation and used to be regarded as the surface work-function. By the old statistics, it differs from $(b_A - b_B)$ by the amount of the internal potential-difference between the metals across the junction 1. Perhaps this difference between the consequences of the two theories could be tested by experiment.

Theory of the Thermoelectric Phenomena

We turn now to the problem of evaluating the rate of generation of heat in a metal through which an electric current is flowing, and in which (according to these theories) there is an intrinsic electric potential-gradient due to a temperature-gradient, or to a gradient of electron-concentration, or both together. The process leads to formulæ which can be tested by experiment, furnishing thus some additional ways of finding out whether these ideas of the new statistics, of the perturbed distribution-function and of the internal electric field are justifiable.

The expression for the rate of generation of heat per unit volume in a conductor traversed by currents of electricity and heat flowing along the axis of x and having current-densities J and W respectively, is $(JE - dW/dx)$. Here E stands for the electric field—not in general for the applied electric field alone, but for the sum of this and the hypothetical internal field. I denote the corresponding acceleration by α, as before, and the rate at which heat is generated per unit volume by r; then:

$$-r = (m\alpha/e)J - dW/dx. \tag{138}$$

The current-density of heat is given by the formula (115), which I repeat:

$$W = \tfrac{1}{2}m \int v^4 \cos^2 \theta g d\tau. \tag{139}$$

Here g stands as always for the non-isotropic perturbation-term in the distribution-function. This and the acceleration α are to be determined from the two equations,

$$\alpha(df_0/d\xi) + \xi(df_0/dx) = (v\xi/l)g = (v^2 \cos \theta/l)g; \tag{140}$$

$$J/e = \int \xi^2 g d\tau = \int v^2 \cos^2 \theta g d\tau, \tag{141}$$

which are the same as (117) and (118) except that the electric current is no longer set equal to zero.

Multiply both sides of (140) by $\frac{1}{2}mv^2 \cos \theta$, and integrate over the entire velocity-space. The integral of the right-hand member is W/l; developing the integral of the left-hand member, we find:

$$W = \tfrac{1}{6}ml(-4\alpha n\bar{v} + d(n\overline{v^3})/dx). \tag{142}$$

Multiply both sides of (140) by $\cos \theta$, and integrate over the entire velocity-space; the integral of the right-hand member is J/le; developing the integral of the left-hand member, we get the equation of which (127) was a special case, to wit:

$$-2\alpha n\overline{v^{-1}} + d(n\bar{v})/dx = 3J/el. \tag{143}$$

Evidently these equations suffice to translate (138) into an expression for r in terms of the mean free path, the universal constants, and the averages of various powers of v.

Postulating the Maxwell-Boltzmann distribution-function for f_0; working out the expressions for α and for dW/dx, and importing the formulæ for σ (equation 114a) and κ (equation 119), one finds:

$$\begin{aligned} J(m\alpha/e) &= J \cdot \frac{1}{2}\frac{k}{e}\frac{dT}{dx} - \frac{J^2}{\sigma} \\ dW/dx &= \frac{d}{dx}\left(\kappa\frac{dT}{dx}\right) + 2J\frac{k}{e}\frac{dT}{dx}, \end{aligned} \tag{144}$$

so the value predicted for the rate of generation of heat per unit volume amounts to this:

$$r = +\frac{J^2}{\sigma} + \frac{d}{dx}\left(\kappa \frac{dT}{dx}\right) + \frac{3}{2}\frac{k}{e}\frac{dT}{dx}J. \tag{145}$$

The first term is obviously the Joule heat; the second is not directly a consequence of this current-flow, as it would occur whatever the agency which set up the temperature-distribution in question. It is the third term which concerns us; this is a "reversible heat," proportional to the first power of the current, so that when the current flows in one sense heat is absorbed and when it is reversed heat is evolved. The sign is such, that heat is absorbed when the electrons are flowing towards the hotter part of the metal; the magnitude is such, that as the electrons move onward they acquire just enough energy to raise their temperature to that of the regions which they enter. The coefficient of this term therefore represents the specific heat of the electron-gas, which is the same as that of any other monatomic gas when referred to equal numbers of particles.

Adopting instead the Fermi distribution, and inserting into (142) and (143) the values of $\bar{v}$ and $\overline{v^{-1}}$ and $\overline{v^3}$ prevailing at absolute zero, we find on making the substitutions in the expression (138) for r that the terms containing the first power of J balance one another out. This might have been expected; for we have just seen that these terms form a sum which is proportional to the specific heat of the electron-gas; and if this result may be extended to an electron-gas conforming to the Fermi distribution, then since the specific heat vanishes at zero so also must this "reversible heat." Working through the second approximation, Sommerfeld found that the net coefficient of the term in J in the expression for r is in fact proportional to the specific heat of the electron-gas, being therefore proportional to T, and given by the formula:

$$\frac{2\pi^2}{3}\frac{mk^2}{eh^2}\left(\frac{2\pi G}{3n}\right)^{2/3} T. \tag{146}$$

Now it is a fact of experience that when an electric current flows along a uniform wire of uneven temperature, heat is generated at a rate which involves a term proportional to the current and which changes sign when the current changes sense. This "Thomson heat," like the maximum value which experiments allow us to admit for the specific heat of the electron-gas, has always been much smaller than the value which the classical statistics requires provided that the free electrons are about as numerous as the atoms. For the Thomson heat as for the specific heat, the new statistics sharply reduces the amounts demanded—to about one per cent of those on which the classical theory insists, at room-temperature that is to say and assuming always that the free electrons are equal in number to the atoms. Agreement in order of magnitude is now attained, and for some metals the advantage is possibly greater; there are indications, too, that the Thomson heat is proportional to T over wide ranges of temperature.

Finally we consider the "Peltier heat"—a term proportional to the current and changing sign when the current changes sense, observed when there is a flow of electricity across a weld or area of contact between two metals. This is clearly to be interpreted as a term in the first power of J, occurring when into the combination $J(m\alpha/e)$—all that remains of the expression (138) for r, when the gradient of temperature is annulled—we substitute the value of α derived from (143) with the assumption that n varies continuously across the weld from the value appropriate to the one metal to the value appropriate to the other. Using the classical statistics, we find that there is such a term; denoting by n and n_0 the electron-concentrations in the two metals, we find for its value:

$$(kT/e) \log (n/n_0)J. \tag{147}$$

Its value for unit current is obviously the intrinsic potential-difference between the metals. Using instead the new statistics, we find that at the absolute zero there is no such term; we must proceed to the next approximation, doing which, Sommerfeld obtained the expression:

$$\frac{2\pi^2}{3}\frac{m(kT)^2}{eh^2}\left[\left(\frac{4\pi G}{3n}\right)^{2/3} - \left(\frac{4\pi G}{3n_0}\right)^{2/3}\right]. \tag{148}$$

Putting the current equal to unity, we find a value very considerably smaller than the intrinsic potential-difference between the metals—a fraction of a millivolt. This is the order of magnitude of the Peltier heat as it is actually observed in many cases. Curiously enough, this fact by itself is in accord with both the theories. By the classical statistics, the intrinsic potential-difference between two metals is generally small, and the Peltier heat for unit current gives its value directly; by the Fermi statistics, the intrinsic potential-difference is generally large, but the Peltier heat for unit current is only a small fraction of it.

Omissions

Among the subjects omitted from this article there are several of much interest, which the reader may trace from the annexed bibliography; in particular:

Sommerfeld's theory of the Hall effect;

Houston's extension of Sommerfeld's theory of intrinsic potential difference, including especially an explanation of the Peltier heat arising when current flows between two differently-oriented crystals of a single substance;

Bloch's use of the new methods of quantum mechanics to make allowance for the influence of the atoms on the conduction-electrons;

Fermi's application of statistical methods to the problem of determining the distribution of electrons in the individual atom;

Fuerth's work on the fluctuations in the new statistics.

The bibliography will indicate other interesting advances in a variety of problems.

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