of molybdenum, found that when molybdenum which had been heated to a certain temperature was raised to a higher temperature its emissivity immediately dropped, then gradually rose to its original value. If the emissivity of filament H were rising during this early period, and, therefore, its temperature at constant brightness were dropping, one would indeed have a rather rapid decrease in V^3I until the emissivity reached its final value. This does not explain, however, why the various curves for H should differ from the corresponding curves for the other filaments.

In conclusion, the data show that there is a definite decrease in V^3I with time, though quantitatively the results obtained from the various filaments do not agree. No explanation has been found for the differences between the various filaments on the basis of the available data. It would seem necessary, in view of the results, to reconsider previous work in which constancy of V^3I was assumed.

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On the Calculation of the Distribution Function

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The distribution function for particles confined to a large circle is found for a repulsive potential of long range. The distribution function is calculated exactly from the Boltzmann-Gibbs equation, and compared with the solution of an implicit equation of the type used by Debye and Hückel in the theory of electrolytes. The solution of the Debye-Hückel equation agrees, for our particular potential, only fairly well with the exact distribution function.

I.

ALTHOUGH the problem of classical statistical mechanics is, in principle, solved by the Boltzman-Gibbs equation

$$P(x_1, y_1, z_1, \cdots x_n, y_n, z_n)dx_1\cdots dz_n = \exp(-\beta V)dx_1\cdots dz_n \qquad (1)$$

for the probability of the configuration characterized by the rectangular coordinates x_1, y_1, z_1, $\cdots$, x_n, y_n, z_n, the answering of questions of immediate physical interest meets, in most cases, serious mathematical difficulties. In (1), $\beta=1/kT$ and V is the potential energy

$$V=\sum_{i<k} v(|r_i-r_k|), \qquad (1a)$$

which we shall assume to be the sum of interactions between pairs.

Many of the quantities of immediate physical importance depend on the distribution function $g(r)$, i.e., on the probability of a distance r between, say, the particles 1 and 2. This is given by

$$g(|r_1-r_2|)=\text{const.}\int\cdots\int \exp(-\beta V) \times dx_3dy_3dz_3\cdots dx_ndy_ndz_n. \qquad (2)$$

However, one can evaluate (2) easily only in the case of dilute matter, i.e., gases. For condensed material, the integrations in (2) are so difficult that indirect methods had to be devised for the evaluation of the distribution function. These methods have two features in common: (a) they do not give g directly but only as the solution of an implicit equation the solving of which, though in most cases not very easy, is still less difficult than the integrations of (2); and (b) the implicit equation for g is not exact, i.e., its solution is only an approximation to the rigorous expression (2). The first implicit equation was given by Debye and Hückel[1] in their theory of electrolytes. More rigorous equations are due to Kirkwood[2] and Mayer.[3]

The present authors became interested in these methods because integrals of the type (2) occur in the theory of the so-called correlation energy. The present note deals with a special problem in which all particles are confined to a large circle of length L; and in which the potential between a pair of particles is given by

$$\beta v(x) = -\ln \sin^2 \pi x/L, \tag{3}$$

where x is the distance between the particles, measured along the circle. We found that for this interaction the distribution function can be evaluated exactly by (2), and that the implicit equation corresponding to Debye and Hückel's theory also can be solved. The comparison of the two results gives an indication of the accuracy of the Debye-Hückel equation (5) for the case of a repulsive potential of long range. In the case of long range forces the Debye-Hückel equation can be expected to give good results.

In the Debye-Hückel theory the distribution function is given, apart from a constant, by an average potential U

$$\ln g(x) = -\beta U(x) + C. \tag{4}$$

The average potential contains the potential $v(x)$ of the original particle around which we investigate the distribution of the others, and the average field of the other particles. There are $g(x')dx'$ particles at a distance x' from the original particle; and their potential, at x, is given by $g(x')dx'v(x-x')$. Hence

$$U(x) = v(x) + \int g(x')v(x-x')dx' \tag{4a}$$

and the implicit equation becomes

$$\ln g(x) = -\beta v(x) - \beta \int g(x')v(x-x')dx' + C. \tag{5}$$

The constant C is determined by the condition that the integral of g must be $n-1$,

$$\int g(x)dx = n-1. \tag{5a}$$

In most cases g is a constant if x is large compared to the average distance between neighboring particles. One can, therefore, substitute

$$g(x) = g_0(1+h(x)), \tag{6}$$

in which $h(x)$ vanishes for large x. Substitution of (6) into (5) gives a somewhat different form to the implicit equation

$$\ln(1+h(x)) = -\beta v(x) - g_0\beta \int h(x')v(x-x')dx' + C', \tag{6a}$$

since the integral of $g_0 v(x-x')$ is independent of x.

II.

The calculations remain to be done. For evaluating (2) we can write

$$\begin{aligned}\exp(-\beta V) &= \prod_{i<k} \sin^2 \pi(x_i - x_k)/L \\ &= 2^{-n(n-1)} \Big| \prod_{i<k} (\exp 2\pi i x_i/L - \exp 2\pi i x_k/L) \\ &\qquad \times \exp(-\pi i(x_i + x_k)/L) \Big|^2. \end{aligned} \tag{7}$$

The factor $\exp(-\pi i(x_i+x_k)/L)$ may be omitted since its absolute value is 1. If we write

$$\omega_i = \exp 2\pi i x_i/L, \tag{7a}$$

we get

$$\exp(-\beta V) = 2^{-n(n-1)} \Big| \prod_{i<k} (\omega_i - \omega_k) \Big|^2, \tag{7b}$$

the product on the right can be written as a determinant $\Delta = |\Delta_{il}|$ where

$$\Delta_{il} = \omega_i^{\,l} = \exp 2\pi i l x_i/L \quad (l = 0, 1, 2, \cdots n-1). \tag{8}$$

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[1] P. Debye and E. Hückel, Physik. Zeits. **24**, 185, 305 (1923); P. Debye, Physik. Zeits. **25**, 97 (1924).

[2] J. G. Kirkwood and Elizabeth Monroe, J. Chem. Phys. **9**, 514 (1941); J. G. Kirkwood, J. Chem. Phys. **3**, 300 (1935).

[3] J. E. Mayer and E. Montroll, J. Chem. Phys. **9**, 2 (1941); J. E. Mayer and S. F. Harrison, J. Chem. Phys. **6**, 87 (1938).

This gives

$$\exp(-\beta V)=2^{-n(n-1)}\Delta\Delta^*. \qquad (9)$$

The determinant $|\Delta_{il}|$ is, in case of odd n, apart from a factor $\exp -\pi i(n-1)(x_1+\cdots+x_n)/L$, the wave function of a one-dimensional degenerate Fermi gas.

One can integrate (9) immediately by developing both Δ and Δ^* with respect to the two rowed minors of the first two rows. The minor of the l_1l_2 columns in Δ is

$$\exp 2\pi i(l_1x_1+l_2x_2)/L \\ -\exp 2\pi i(l_2x_1+l_1x_2)/L. \qquad (10)$$

Its cofactor is orthogonal to the cofactor of every two rowed minor of Δ^*, excepting the cofactor of the minor of the l_1l_2 columns. The product of the cofactors of the l_1l_2 minors of Δ and Δ^* gives $(n-2)!$ if integrated over $x_3, \cdots, x_n$. Thus

$$\int\cdots\int \exp(-\beta V)dx_3\cdots dx_n \\ =\sum_{l_1<l_2} 2^{-n(n-1)}(n-2)!\,|\exp 2\pi i(l_1x_1+l_2x_2)/L \\ -\exp 2\pi i(l_2x_1+l_1x_2)/L\,|^2. \qquad (10a)$$

This is, according to (2), proportional to $g(x_1-x_2)$. The sum in (10a) can be readily evaluated and gives, with (5a),

$$g(x)=\frac{n}{L}\left(1-\frac{\sin^2 \pi nx/L}{n^2\sin^2 \pi x/L}\right) \\ \approx\frac{n}{L}\left(1-\frac{\sin^2 \pi nx/L}{\pi^2n^2x^2/L^2}\right). \qquad (11)$$

The last expression is valid if x remains of the order of magnitude of the average distance of two particles, i.e., is not very much larger than L/n. Equation (11) gives the rigorous expression for g; it is the lowest curve in Fig. 1. The abscissae in this figure are $n\pi x/L$ so that the average distance of two particles corresponds to the abscissa π in the graph. The ordinates are multiplied by L/n.

That the solution of the Debye-Hückel Eq. (5) is different from (11), can be seen by inserting (11) and (3) into the right side of (5). If $g'(x)$ is the value of $g(x)$ obtained by these substitutions, this gives

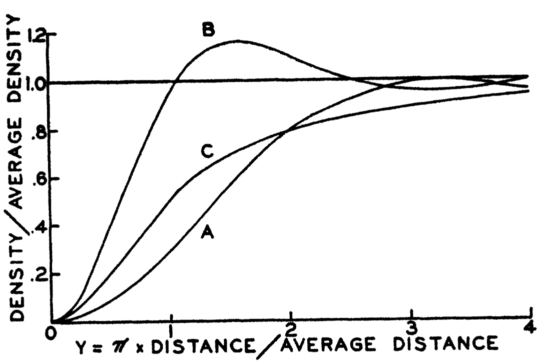

FIG. 1. Distribution functions. The ordinates are the distribution function $g(x)/(n/L)$ representing the density of particles divided by the average density. The abscissae are $y=\pi nx/L$, π times the distance divided by the average distance of nearest neighbors. The distance is equal to the average distance for the abscissa $y=\pi$. Curve A represents the rigorous value of the distribution function $g(x)/(n/L)$ given by (11) from the Boltzmann-Gibbs equation. Curve B represents the distribution function, $g'(x)$ of (12a), obtained by inserting the rigorous value (11) in the right-hand side of the Debye-Hückel Eq. (5). Curve C represents the distribution function (13) obtained by solving the Debye-Hückel equation.

$$\ln g'(x)=-\frac{\sin 2\pi nx/L}{\pi nx/L}+2Ci(2\pi nx/L) \qquad (12)$$

or

$$g'(x)=\exp\left[-\frac{\sin 2\pi nx/L}{\pi nx/L}+2Ci(2\pi nx/L)\right]. \qquad (12a)$$

$g'(x)$ is the uppermost curve in Fig. 1. If (11) were a solution of (5), the value of $g'(x)$ in (12a) would be equal to the rigorous value of $g(x)$ given by (11); and the uppermost curve of Fig. 1 would coincide with the lowest curve. One sees that this is far from being true. The evaluation of the integral obtained by inserting (11) and (3) into (5), i.e., the derivation of (12), requires a somewhat lengthy calculation and will not be given in detail. Ci in (12) is the cosine integral as defined in Jahnke-Emde.[4]

One would expect, on the basis of the lowest and highest curves in Fig. 1, that the solution of (5) would be represented by a curve similar to the middle one of the figure. This corresponds to

$$g(x)=\frac{n}{L}\left(1-\frac{1}{1+n^2\sin^2 \pi x/L}\right) \qquad (13)$$

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[4] E. Jahnke and F. Emde, *Tables of Functions* (B. G. Teubner, 1933), second edition.

and the following calculation shows that (13) is indeed the solution of (5) for the potential (3). In order to show this, one can first verify (5a), using the assumption $n\gg 1$, and then calculate

$$I=-\beta\int g(x')v(x-x')dx'$$

$$=\frac{n}{L}\int_0^L\left(1-\frac{1}{1+n^2\sin^2\pi x'/L}\right)\times\ln\sin^2\pi(x-x')/Ldx'. \tag{13a}$$

The first term is a well known definite integral; its value is $-2n\ln 2$. In order to integrate the second term, one can change the limits of integration and integrate from $-\frac{1}{2}L$ to $\frac{1}{2}L$. Then the first factor will be very small, except for very small x' for which the sine can be replaced by its argument. Thus (13a) becomes

$$I=-2n\ln 2-\frac{n}{L}\int_{-\frac{1}{2}L}^{\frac{1}{2}L}\frac{\ln\sin^2\pi(x-x')/L}{1+\pi^2n^2x'^2/L^2}dx'. \tag{13b}$$

If x is of the order of L, the remaining integral will have two maxima: at $x'=0$ and at $x'=x$. However, the integral over the second maximum is inversely proportional to n and can be neglected. The integral over the first maximum becomes, if one replaces $x-x'$ by x in the numerator

$$I=-2n\ln 2-\ln\sin^2\pi x/L \quad \text{for } x\gg L/n. \tag{13c}$$

If x is not large as compared with L/n, the sine can be replaced by its argument in (13b) since the denominator becomes very large for $x'\gg L/n$. This gives, with $y'=\pi nx'/L$ and $y=\pi nx/L$,

$$I=-2n\ln 2-\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\ln(y-y')^2/n^2}{1+y'^2}dy'$$

$$=-2n\ln 2+\ln n^2-\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\ln(y-y')^2}{1+y'^2}dy' \tag{13d}$$

and

$$\frac{\partial I}{\partial y}=-\frac{2}{\pi}\int_{-\infty}^{\infty}\frac{dy'}{(1+y'^2)(y-y')}=-\frac{2y}{1+y^2}, \tag{13e}$$

since the main value of the integral has to be taken in (13e). We now have

$$I=-2n\ln 2+\ln n^2-\ln(1+y^2)$$

$$-\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\ln y'^2}{1+y'^2}dy'. \tag{13f}$$

In the last integral the lower limit can be replaced by 0 if a factor 2 is inserted. Substitution then of z for $\ln y$ shows that the integral in (13f) vanishes and we have

$$I=-2n\ln 2+\ln n^2-\ln(1+\pi^2n^2x^2/L^2)$$

$$\text{for } x\ll L. \tag{13g}$$

Since $n\gg 1$,

$$I=-\beta\int g(x')v(x-x')dx'=-2n\ln 2$$

$$+\ln n^2-\ln(1+n^2\sin^2\pi x/L) \tag{14}$$

holds for both regions (13c) and (13g). Insertion of (13), (14), and (3) into (5) shows that (5) is indeed satisfied by (13). C in (5) has the value $\ln 2^{2n}n/L$. The solution (13) of (5) is shown in Fig. 1 lying for small abscissae between the other two curves.

III.

One sees that the solution of the Debye-Hückel equation agrees fairly well with the correct distribution function if the potential is given by (3). In particular, the total volume of the "hole" in the distribution function is 1 in both cases. Nevertheless, (5) gives too high a probability of a close approach of two particles since (13) is too high for small abscissae. The failure of (5) in this respect could have been foreseen and depends only on the repulsive character of our potential (3). What is essentially neglected in (5) is that the particle under consideration, particle 2 in our notation, has an effect on the rest of the particles. In our case, it pushes them away from itself so that the distribution of the particles 3, 4, $\cdots$, n will, in reality, show a hole around the point where particle 2 is. Thus particle 2 will be under a lower potential than the average potential U given by (4a). However, the difference between the actual and the average potential is smallest for small x because, where the second particle is close to the first, there are very few particles to be shoved away from its neighborhood.