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The Theory of Liquid Helium

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The free energy, F, of an assembly of interacting helium atoms is expressed in terms of the trace of the density operator, exp $(-\beta H)$, where $\beta=1/kT$, H is the Hamiltonian and T the temperature. The Hamiltonian is written as H_0+gW, where H_0 is the part corresponding to the kinetic energy and gW the potential energy. The resulting expression for F is expanded in powers of g, the first two terms of the series being calculated explicitly. The first term, which is independent of g, gives the free energy of the London theory, and leads to all the usual results. In particular the transition at the lambda temperature, T_λ, is of the third order. The second term in the expansion of F raises the transition to one of the second order; all the second-order derivatives of this term are discontinuous at T_λ, while T_λ and $\partial T_\lambda/\partial\rho$ are the same as in the London theory. Numerical values are obtained for the specific heat and the discontinuity in the specific heat. These are compared with experiment and it is found that there is an improvement as compared with previous theories.

I. INTRODUCTION

The theories of liquid helium that have so far been proposed, lead in some measure to an understanding of the lambda transition, and of the anomalous behavior below the lambda temperature. These theories are usually divided into two types according as to whether they explain the problem presented by a liquid, in terms of a gaseous model, or in terms of a solid model. They are generally associated with the names of London and Landau, respectively. Recently Temperley[1] has compared these two types of theories in a general manner. He concludes that the London type of theory is more satisfactory near the lambda temperature, while the Landau type gives better results at low temperatures, particularly near absolute zero. This is, of course, exactly what might be expected from the different assumptions inherent in the two approaches.

The original model proposed by London[2,3] was, however, very crude in that the mutual interactions between the helium atoms were not taken into account. The purpose of this paper is to present an extension of this thoery in which this defect is partly remedied. There have been several attempts to improve the original theory. The first was by London himself.[4] This was based on the assumption that the density of single-particle states, with wave vectors **k**, lying between **k** and $\mathbf{k}+d\mathbf{k}$, was to depend not on k^2dk but on $k^\gamma dk$. The constant, γ, was determined so that the lambda transition became a second-order transition. The results of this assumption are too well known,[4–6] to require any elaboration. For our purpose it is sufficient to note that the assumption has never been justified theoretically. Schiff[7] showed that London's theory was the first-order term in a "quasi" virial expansion of the partition function. He calculated the next term but found that there was practically no improvement over the original theory. Such an expansion is necessarily divergent for a liquid phase in any case. Other treatments have been given by Bijl, de Boer, and Michels,[8] Goldstein,[9] and Matsubara.[10] All these theories, however, contain assumptions of an arbitrary nature, which have not so far been justified. In what follows, a new mode of analysis will be given. This consists in expanding the free energy F, in powers of a coupling constant g. The way in which g enters into the theory is readily seen if the hamiltonian of the system, H, is written in the form,

$$H=H_0+\sum_{i<j} g\omega(r_{ij}),\qquad r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|, \tag{1.1}$$

where H_0 is the kinetic energy of the system, and the other term in Eq. (1.1) is the potential energy due to the interactions between the helium atoms, the positions of which are given by the vectors $\mathbf{r}_i$. By using Eq. (1.1), the free energy may be written in the form

$$F=\sum_{n=0}^{\infty} g^n F_n, \tag{1.2}$$

where the F_n are independent of g. We shall calculate F_0 and F_1, only.

We can employ our theory to interpret the experimental facts in two different ways, which may be termed loosely the qualitative and quantitative aspects. If we make g very small then we might expect that the first two terms in Eq. (1.2) would give an accurate account of the behavior of a weakly coupled Bose-Einstein assembly. This aspect of the theory is of importance, as considerable doubt has been thrown on

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London's original theory.[11,12] These doubts arise from the fact that it is difficult to see how the behavior of a liquid can be represented in any way by means of an ideal gas. Indeed, many have considered the qualitative agreement of the theory with experiment to be no more than fortuitous. Thus as our theory takes into account, in a rigorous manner, the first order departures from the ideal gas model, it should provide evidence for or against London's theory. Quantitatively we can compare the result of the theory with experimental data, using for g the value determined by de Boer[13] from calculations of the second virial coefficient of helium at higher temperatures.

In the next section the terms F_0 and gF_1 in Eq. (1.2) are calculated. The result is expressed in terms of a general interaction potential between the particles in the assembly. In carrying out this calculation in detail certain approximations are made; with these approximations it becomes obvious that the lambda temperature itself, and the dependence of the lambda temperature on the density, are the same as in London's theory.[6] In the third section the thermodynamic properties of the model are investigated from a qualitative point of view. It is found that all three second-order derivatives of F, with respect to T and V, are discontinuous at the lambda temperature. This is in agreement with experiment,[14] and marks a definite improvement over the London theory. Computations of the specific heat have been carried out for two types of interaction, and the results are compared with experiment in Sec. 4. With de Boer's potential,[13] it is found that the shape of the specific heat curve below the lambda temperature is now much nearer that found experimentally. The magnitude of the specific heat at the lambda temperature is correct, for very reasonable values of a parameter r_0 which appears in the theory. The sign of the discontinuity in the specific heat is, however, opposite to that found experimentally. If, however, we use a potential that approximates closely to the potential of the *mean* force between helium atoms, then the break in the specific heat has the correct sign, while the results below the lambda temperature are unaltered. Thus we can conclude that both qualitatively and quantitatively the model gives results which are an improvement over previous theories. Unfortunately it does not seem possible to calculate explicitly any of the higher order terms in Eq. (1.2).

II. THE EXPANSION OF THE FREE-ENERGY

Consider an assembly of N helium atoms each of mass m in a rectangular box of volume V. We write Eq. (1.1) in the form,

$$H=\sum_{i=1}^{N}\mathbf{p}_i^2/2m+gW, \tag{2.1}$$

where $\mathbf{p}_i$ is the momentum of the ith particle, and gW is the potential energy of the system. The analysis that is required, to expand F in powers of g, has been developed in a previous publication.[15] It was shown there that the partition function, and hence, the free energy, may be expanded in powers of g provided that either (a) the potential energy $\omega(r_{ij})$ has no singularities at which it becomes positively infinite, or (b) that $\omega(r_{ij})$ represents the interactions between particles that have finite incompressible cores. If, however, the potential energy is positively infinite only at isolated points then it is impossible to expand the free energy in this manner. The case where $\omega(r_{ij})$ becomes negatively infinite is of no physical interest and will not be considered. Quite generally it is clear that the potential energy of any two atoms or molecules must become very large and positive, and eventually infinite, whenever the two particles approach sufficiently close to one another. Therefore, if we wish to expand the free energy for an assembly of helium atoms in powers of g, then we must assume that they have finite incompressible cores. This seems to be perfectly justified, and such potentials have been used in many previous calculations. Thus, $\omega(r_{ij})=+\infty$ for $|\mathbf{r}_i-\mathbf{r}_j|=r_{ij}\leq 2r_0$, where r_0 is the radius of the incompressible core. We now use the formulas developed in I; the partition function Z is given by

$$Z=Z_0+gZ_1+O(g^2), \tag{2.2}$$

where, in Eq. (2.2),

$$Z_0=\sum_l G_l\exp(-\beta E_l), \tag{2.3}$$

and

$$Z_1=-\beta\sum_l G_l W_{ll}\exp(-\beta E_l). \tag{2.4}$$

In Eqs. (2.3) and (2.4), G_l is the number of states associated with the energy level E_l, and W_{ll} is given by

$$W_{ll}=\int_{S_1}\chi_l^* W\chi_l d\mathbf{r}_1\cdots d\mathbf{r}_N. \tag{2.5}$$

The functions χ_l in Eq. (2.5) are the correctly symmetrized solutions of the wave equation for N perfectly elastic spheres, the E_l being the corresponding eigenvalues. The above equations are equivalent to Eqs. (1.17) and (4.16) of I. The free energy F is given by

$$F=-\beta^{-1}\log Z. \tag{2.6}$$

Consequently, to the first order in g,

$$F=-\beta^{-1}\log Z_0-g\beta^{-1}Z_1/Z_0. \tag{2.7}$$

From Eqs. (2.7) and (1.2) it follows at once that

$$F_0=-\beta^{-1}\log[\sum_l G_l\exp(-\beta E_l)], \tag{2.8}$$

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and

$$F_1=\sum_l G_l W_{ll}\exp(-\beta E_l)/\sum_l G_l\exp(-\beta E_l). \qquad (2.9)$$

We notice that since F_0 depends on r_0, it is *not* independent of the parameters specifying the interaction potential. It is probably impossible to evaluate either G_l or W_{ll} rigorously, and to made further progress it is necessary to find suitable approximations for them. In the case of helium the radius of the incompressible core r_0 has a value of about $1\cdot 1\times 10^{-8}$ cm. Furthermore the volume available to each atom V/N is, at the densities we are interested in, about 5×10^{-23} cm^3. On the other hand, the volume of the incompressible core is about 5×10^{-24} cm^3. We shall therefore make the approximation of replacing G_l in Eqs. (2.3) and (2.4) by G_l^0, its value for the free-particle system. To this degree of approximation, F_0 is the free energy of an ideal Bose-Einstein gas. We next make the approximation of replacing the elastic sphere wave functions χ_l in Eq. (2.5) by the correctly symmetrized free-particle wave functions Ψ_l. The region of integration S_1 is, for the moment, left unaltered. This insures that W_{ll} remains finite. From Eqs. (1.1) and (2.5) it is seen that W_{ll} is the sum of a number of terms of the form $\int_{S_1}\omega(r_{ij})\times d\mathbf{r}_1\cdots d\mathbf{r}_N$. In each of these terms we shall make the further approximation of extending the restricted integrations over the coordinates that do not appear in the potential function, $\omega(r_{ij})$, to cover the entire volume. The integrations over the coordinates that do appear in the potential function are still to be restricted to that region of configuration space, for two molecules, such that $r_{ij}>2r_0$. It does not seem to be worth while investigating more refined approximations until the results of these very simple ones have been established.

With these approximations, F_0 and F_1 become

$$F_0=-\beta^{-1}\log\sum_l G_l^0\exp(-\beta E_l), \qquad (2.10)$$

$$F_1=\sum_l G_l^0 W_{ll}\exp(-\beta E_l)/\sum_l G_l^0\exp(-\beta E_l). \qquad (2.11)$$

An explicit expression has been given for F_0 by London.[16] We shall therefore confine our attention to F_1. The function W_{ll}, to our degree of approximation, can easily be calculated in the usual manner. It is given by

$$W_{ll}=\tfrac{1}{2}\sum_{\mathbf{k}\neq\mathbf{k}'}\sum n_{\mathbf{k}}n_{\mathbf{k}'}K_{\mathbf{k},\mathbf{k}'}+\frac{N(N-1)}{2}K_0. \qquad (2.12)$$

The symbols $n_{\mathbf{k}}$ in Eq. (2.12) are the set of numbers that define the state l. That is the state of the system is taken as being defined by the set of numbers, $(n_{\mathbf{k}})$, that specify the number of particles with wave vectors $\mathbf{k}$. The $n_{\mathbf{k}}$ run from 0 to N and satisfy the relation

$$\sum_{\mathbf{k}}n_{\mathbf{k}}=N. \qquad (2.13)$$

The function $K_{\mathbf{k},\mathbf{k}'}$ is given by

$$K_{\mathbf{k},\mathbf{k}'}=V^{-2}\iint_{|\mathbf{r}_1-\mathbf{r}_2|>2r_0}\omega(r_{12})\times\exp[-2\pi i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{r}_1-\mathbf{r}_2)]d\mathbf{r}_1d\mathbf{r}_2 \qquad (2.14)$$

while $K_0=K_{\mathbf{k},\mathbf{k}}$ and is thus independent of $\mathbf{k}$. Combining Eqs. (2.11) and (2.12), we obtain

$$F_1=\tfrac{1}{2}\sum_{\mathbf{k}\neq\mathbf{k}'}\sum \bar{n}_{\mathbf{k}}\bar{n}_{\mathbf{k}'}K_{\mathbf{k},\mathbf{k}'}+\frac{N(N-1)}{2}K_0. \qquad (2.15)$$

The $\bar{n}_{\mathbf{k}}$ are the mean values of the $n_{\mathbf{k}}$ that appear in Eq. (2.12), the means having been taken with the free particle weights $\exp(-\beta E_l)G_l^0/Z_0$. They are therefore identical with the free-particle occupation numbers of a Bose-Einstein gas, and from Eq. (2.13) satisfy the relation $N=\sum_{\mathbf{k}}\bar{n}_{\mathbf{k}}$. Now it is this relation that defines T_λ and $\partial T_\lambda/\partial\rho$, where ρ is the density. Both these quantities will consequently be identical with those of the ideal gas approximation. This last statement brings out the essential nature of the approximation of replacing G_l by G_l^0. If this had not been done, F_0 would have been dependent on r_0 and therefore the zero-order approximation to T_λ and $\partial T_\lambda/\partial\rho$ would have been dependent on r_0, and would be different from the values they have in the ideal gas approximation. Thus, if a more accurate evaluation of G_l could be carried out, it should be possible to obtain a value of T_λ nearer to that found experimentally. For convenience we list the properties of the $\bar{n}_{\mathbf{k}}$:

$$\left.\begin{aligned}&\bar{n}_{\mathbf{k}}=[\exp(\lambda k^2+\alpha)-1]^{-1},\ \text{all }\mathbf{k};\quad T>T_\lambda,\\&\bar{n}_{\mathbf{k}}=[\exp(\lambda k^2)-1]^{-1},\ \mathbf{k}>0;\quad T<T_\lambda,\\&\bar{n}_0=N-\sum_{\mathbf{k}\neq 0}\bar{n}_{\mathbf{k}};\quad T<T_\lambda.\end{aligned}\right] \qquad (2.16)$$

In Eq. (2.16) $\lambda=h^2/2mkT$, where k is Boltzmann's constant. The statistical parameter α is determined, as a function of T and V, for $T>T_\lambda$, by the relation $\sum_{\mathbf{k}}\bar{n}_{\mathbf{k}}=N$. For $T\leq T_\lambda$ α is identically zero. The condensation temperature T_λ is given by

$$T_\lambda=(h^2/2m\pi k)[N/V\zeta(\tfrac{3}{2})]^{\frac{2}{3}}, \qquad (2.17)$$

where $\zeta(\frac{3}{2})$ is the Riemann zeta function of order $\frac{3}{2}$.

It is convenient to reduce F_1 to a still more explicit form. In Eq. (2.15) we replace the $K_{\mathbf{k},\mathbf{k}'}$ by their average values, the averaging being done over all angles in $\mathbf{k}$ and $\mathbf{k}'$ space. This is legitimate because we are eventually going to replace the summations in (2.15) by integrations, and the only angular dependence comes from the $K_{\mathbf{k},\mathbf{k}'}$; the $\bar{n}_{\mathbf{k}}$ depend only on $|\mathbf{k}|$. This means that we can carry out the angular part of the integrations at once. Thus, dropping the irrelevant constant, F_1 becomes

$$F_1=\tfrac{1}{2}\sum_{|\mathbf{k}|\neq|\mathbf{k}'|}\sum\bar{n}_{\mathbf{k}}\bar{n}_{\mathbf{k}'}\langle K_{\mathbf{k},\mathbf{k}'}\rangle. \qquad (2.18)$$

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[16] F. London, Phys. Rev. 54, 947 (1938).

In Eq. (2.18),

$$\langle K_{\mathbf{k},\mathbf{k}'}\rangle=\frac{4}{V^2kk'}\iint_{r>2r_0}\omega(r)\sin(2\pi kr)\sin(2\pi k'r)d\mathbf{r}_1d\mathbf{r}_2,$$

where $r=|\mathbf{r}_1-\mathbf{r}_2|$. The above expression can be readily reduced to the form,

$$\langle K_{\mathbf{k},\mathbf{k}'}\rangle=\frac{16\pi}{kk'V}\int_{2r_0}^{\infty}\omega(r)\sin(2\pi kr)\sin(2\pi k'r)dr. \qquad (2.19)$$

The lower limit, $2r_0$, in Eq. (2.19) occurs because in Eq. (2.14) the integrations over $\mathbf{r}_1$ and $\mathbf{r}_2$ are restricted to the region $r_{12}\geqslant 2r_0$. It is now convenient to divide the calculations into two parts corresponding to temperatures below and above the lambda temperature:

(a) $T<T_\lambda$. In this range of temperature we have

$$F_1=F_1^-=\tfrac{1}{2}\sum_{|\mathbf{k}|\neq|\mathbf{k}'|}\sum\bar{n}_{\mathbf{k}}\bar{n}_{\mathbf{k}'}\langle K_{\mathbf{k},\mathbf{k}'}\rangle. \qquad (2.20)$$

When the summations in Eq. (2.20) are replaced by integrations, care must be taken not to suppress the state $|\mathbf{k}|=0$, by using a density of states proportional to k^2, which is zero for $|\mathbf{k}|=0$. This can be avoided by writing,

$$F_1^-=\tfrac{1}{2}\sum_{|\mathbf{k}|\neq|\mathbf{k}'|\neq 0}\sum\bar{n}_{\mathbf{k}}\bar{n}_{\mathbf{k}'}\langle K_{\mathbf{k},\mathbf{k}'}\rangle+\bar{n}_0\sum_{|\mathbf{k}|\neq 0}\bar{n}_{\mathbf{k}}\langle K_{\mathbf{k},0}\rangle. \qquad (2.21)$$

The summations may now be safely replaced by integrations. The states $|\mathbf{k}|=|\mathbf{k}'|\neq 0$ contribute nothing to the double integral. This is because the integrand, and all its derivatives with respect to T and V are measurable on the line $k=k'$, and these points form a set of zero (plane) measure. The quantity $\langle K_{\mathbf{k},\mathbf{k}'}\rangle$ has already been calculated in Eq. (2.19), while $\langle K_{\mathbf{k},0}\rangle$ is given by

$$\langle K_{\mathbf{k},0}\rangle=\frac{8\pi}{kV}\int_{2r_0}^{\infty}\omega(r)r\sin(2\pi kr)dr. \qquad (2.22)$$

Combining Eqs. (2.22) and (2.19) with (2.21) and replacing the summations by integrations, we have

$$F_1^-=8\pi\int_{2r_0}^{\infty}\omega(r)[VI^2+\bar{n}_0rI]dr, \qquad (2.23)$$

where

$$I=\int_0^{\infty}k\sin(2\pi kr)[\exp(\lambda k^2)-1]^{-1}dk. \qquad (2.24)$$

Unfortunately I cannot be calculated in terms of known functions but it can be easily expressed in the form,

$$I=(\pi/\lambda)^{\frac{3}{2}}(r/2)S_3^-, \qquad (2.25)$$

where the functions S_μ^- have been introduced for convenience later; they are defined by,

$$S_\mu^-=\sum_{n=1}^{\infty}\exp(-\pi^2r^2/n\lambda)/n^{\mu/2}. \qquad (2.26)$$

Using these results, together with the relations

$$\bar{n}_0=N(1-\tau^{\frac{3}{2}}),\quad\text{and}\quad(\pi/\lambda_0)^{\frac{3}{2}}=N/V\zeta(\tfrac{3}{2}),$$

where

$$\lambda_0=(\lambda)_{T=T_\lambda},\quad\text{and}\quad\tau=T/T_\lambda,$$

we have finally,

$$F_1^-=P\int_{x_0}^{\infty}x^2\omega(x)$$
$$\times[(\tau^3/2\zeta)(S_3^-)^2+\tau^{\frac{3}{2}}(1-\tau^{\frac{3}{2}})S_3^-]dx, \qquad (2.27)$$

where $x_0=2r_0/\sigma$, $P=4\pi RN\sigma^3/\zeta(\frac{3}{2})kV$, and R is the gas constant. The variable of integration has been changed from r to $x=r/\sigma$, and S_3^- is now given by,

$$S_\mu^-=\sum_{n=1}^{\infty}\exp(-ax^2/n)/n^{\mu/2}, \qquad (2.28)$$

where $a=\pi^2\sigma^2/\lambda$.

(b) $T>T_\lambda$. We now have,

$$F_1=F_1^+=\sum_{|\mathbf{k}|\neq|\mathbf{k}'|}\sum\bar{n}_{\mathbf{k}}\bar{n}_{\mathbf{k}'}\langle K_{\mathbf{k},\mathbf{k}'}\rangle. \qquad (2.29)$$

When we pass to the continuous-spectrum approximation, and replace the summations by integrations using a density of states proportional to k^2, we shall suppress any contributions from terms of the form $\bar{n}_0\sum_{|\mathbf{k}|\neq 0}\bar{n}_{\mathbf{k}}\langle K_{\mathbf{k},0}\rangle$ and $(\bar{n}_0)^2\langle K_{0,0}\rangle$. The latter should not be present in any case, as the summation is over unequal $|\mathbf{k}|$ and $|\mathbf{k}'|$. The former should be present. It is easily seen however, that because $\bar{n}_0$ is of order $N^{2/3}$ these terms are of order $N^{5/3}$ at most, and so are statistically negligible compared with the rest of the sum which is of order N^2. Thus it would not matter whether these terms are present or not, provided that we merely required the function F_1^+. We are, however, concerned not only with F_1^+, but also with its first and second derivatives with respect to T and V, and the derivatives of the suppressed terms are not statistically negligible at the lambda temperature; thus $\partial\bar{n}_0/\partial T$ and $\partial^2\bar{n}_0/\partial T^2$ are both of order N at T_λ. In Eq. (2.29) the $\bar{n}_{\mathbf{k}}$ depend on α, Eq. (2.16), so when F_1^+ is differentiated with respect to T it will also have to be differentiated with respect to α because of the implicit dependence of α on T. Thus terms will arise in the differentiated series which were not present for $T<T_\lambda$. For example, in the first differentiation we get terms of the form $[\exp(\lambda k^2+\alpha)-1]^{-2}$. When we now pass to the continuous spectrum approximation a term such as this will give rise to an integral which diverges, as $\alpha\rightarrow 0$, in the same manner as the series $\sum_{n=1}^{\infty}e^{-n\alpha}/n^{\frac{1}{2}}$ diverges for $\alpha\rightarrow 0$. However all such integrals are multiplied by factors of the form $\partial\alpha/\partial T$,

which go to zero, for $\alpha \to 0$, just sufficiently fast for the product to yield a finite result (Appendix). It is just these terms which make up for the apparent suppression of terms like $\partial \bar{n}_0/\partial T \sum_{|\mathbf{k}| \neq 0} \bar{n}_{\mathbf{k}} \langle K_{\mathbf{k},0} \rangle$. However, terms will now arise in the double sum, which give contributions of the form $(\partial \bar{n}_0/\partial T)^2 \langle K_{0,0} \rangle$ and $(\partial^2 \bar{n}_0/\partial T^2)\bar{n}_0 \langle K_{0,0} \rangle$. These terms should not be present since they arise from terms for which $|\mathbf{k}| = |\mathbf{k}'| = 0$. This difficulty can be easily overcome by writing Eq. (2.29) as,

$$F_1^+ = \tfrac{1}{2} \sum_{|\mathbf{k}| = |\mathbf{k}'|} \sum \bar{n}_{\mathbf{k}} \bar{n}_{\mathbf{k}'} \langle K_{\mathbf{k},\mathbf{k}'} \rangle - \tfrac{1}{2} (\bar{n}_0)^2 \langle K_{0,0} \rangle, \tag{2.30}$$

where in Eq. (2.30) the summation is to be over equal values of $|\mathbf{k}|$ and $|\mathbf{k}'|$, and the second term exactly cancels out the unwanted contributions from the states $|\mathbf{k}| = |\mathbf{k}'| = 0$; the states $|\mathbf{k}| = |\mathbf{k}'| \neq 0$ give no contribution to the integral for the same reason as was given previously for the case $T < T_\lambda$. We may now safely replace the sums by integrations and get

$$F_1^+ = P \int_{x_0}^{\infty} x^2 \omega(x) \tau^3 / 2\zeta (S_3^+)^2 dx - \tfrac{1}{2} (\bar{n}_0)^2 \langle K_{0,0} \rangle, \tag{2.31}$$

where

$$S_\mu^+ = \sum_{n=1}^{\infty} \exp(-ax^2/n - n\alpha)/n^{\mu/2},$$

and τ and P have the same meaning as before.

From Eqs. (2.27) and (2.31), C_{V1}^- and C_{V1}^+ may be calculated, where C_{V1}^- and C_{V1}^+ are the contributions to C_V the specific heat at constant volume from gF_1^- and gF_1^+, respectively; as the calculations were limited to the region $T \leq T_\lambda$ we shall merely quote the result for C_{V1}^-.

$$C_{V1}^- = \frac{P\tau^{\frac{3}{2}} g}{T} \int_{x_0}^{\infty} x^2 \omega(x) \left[\frac{\tau^{\frac{3}{2}}}{\zeta} f_1(x) - f_2(x) \right] dx. \tag{2.32}$$

The functions $f_1(x)$ and $f_2(x)$ are given by

$$\left. \begin{aligned} f_1(x) &= 3S_3^-(2\zeta - S_3^-) - 6zS_5^-(\zeta - S_3^-) \\ &\qquad - z^2(S_5^-)^2 + z^2 S_7^-(\zeta - S_3^-) \\ \text{and} \qquad & \\ f_2(x) &= \tfrac{3}{4} S_3^- - 3zS_5^- + z^2 S_7^-, \end{aligned} \right\} \tag{2.33}$$

where

$$z = ax^2/\lambda \quad \text{and} \quad \zeta = \zeta(\tfrac{3}{2}).$$

The discontinuity in the specific heat can also be calculated from Eqs. (2.27) and (2.31). It is found to be given by

$$\begin{aligned} (\Delta C_{V1}) &= (C_{V1}^+ - C_{V1}^-)_{T=T_\lambda} \\ &= PT_\lambda^2 \zeta^{-1} (\partial^2 \alpha / \partial T^2)_{T=T_\lambda} \int_{x_0}^{\infty} x^2 \omega(x) S_3 \mathcal{S}_{\frac{1}{2}} dx, \end{aligned} \tag{2.34}$$

where

$$\mathcal{S}_{\frac{1}{2}} = \sum_{n=1}^{\infty} [1 - \exp(-ax^2/n)] n^{-\frac{1}{2}},$$

$(\partial^2 \alpha / \partial T^2)_{T=T_\lambda}$ is given in the Appendix, and S_3 is the common value of S_3^- and S_3^+ at T_λ, that is for $\alpha = 0$.

III. THE THERMODYNAMICS OF THE LAMBDA TRANSITION

We shall now use the expressions given by Eqs. (2.11) and (2.18) to deduce the qualitative behavior of the model at the lambda temperature. Our main interest is to determine the nature of the discontinuities in the derivatives of F. These arise from the discontinuities in the derivatives of the $\bar{n}_{\mathbf{k}}$ which in turn depend on the discontinuities in α. As the first-order derivatives of α are all continuous at the lambda temperature (Appendix), it follows that the first-order derivatives of F are continuous at this point. In particular the entropy, $S = -(\partial F/\partial T)_V$ and the pressure, $p = -(\partial F/\partial V)_T$ are continuous at T_λ. To study the second derivatives of F we require the following relations,

$$(\partial F_0 / \partial \alpha) = 0, \tag{3.1}$$

and

$$(\partial F_1 / \partial \alpha) \neq 0. \tag{3.2}$$

Equation (3.1) is equivalent to the relation $N = \sum_{\mathbf{k}} \bar{n}_{\mathbf{k}}$, and follows immediately when F_0 is calculated in the usual manner.[17,18] Equation (3.2) is obvious from the form of Eq. (2.18). It follows from Eq. (3.1) that the nth derivatives of F_0 depend only on the $(n-1)$th derivatives of α. Thus, as the first discontinuous derivatives of α are of the second order, the first discontinuous derivatives of F_0 will be of the *third* order; for example the gradient of the specific heat. This of course is a well known result of the ideal gas approximation. On the other hand, from Eq. (3.2), the nth derivatives of F_1 will depend on the nth derivatives of α, and hence the first discontinuous derivatives of F_1 will be of the *second* order. Now we have

$$C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V; \quad \left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial^2 F}{\partial T \partial V}\right);$$
$$\left(\frac{\partial p}{\partial V}\right)_T = -\left(\frac{\partial^2 F}{\partial V^2}\right). \tag{3.3}$$

Thus, the theory predicts that all three quantities on the left-hand side of relations (3.3) will be discontinuous at T_λ. This is in agreement with experiment, and represents a considerable improvement over the London theory which predicts that all these quantities should be continuous. It should be noted, however, that the experimental values correspond to discontinuities in derivatives of the *total* free energy, whereas we have only examined the behavior of the first and second terms of series (1.2) for F. But it would seem to be purely accidental if the discontinuities arising from the higher order terms in series (1.2) exactly cancelled those of the first two terms.

Our general qualitative conclusions concerning the discontinuities depend directly on the statistics of the

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[17] B. Kahn, dissertation, Utrecht, 1938.

[18] A. R. Fraser, Phil. Mag. **42**, 156, 165 (1951).

particles. They therefore lend considerable support to London's hypothesis that the anomalous behavior of liquid helium is closely connected with the type of statistics obeyed by the helium atoms.

IV. COMPUTATION OF SPECIFIC HEAT—COMPARISON WITH EXPERIMENT

The contribution C_{VI}^{-}, to the specific heat C_V, has been calculated for two types of interaction potential. The first type of potential was identical with that used by de Boer[13] to calculate the second virial coefficient of helium at low temperatures. That is, $g\omega(r)$ was assumed to be given by

$$g\omega(r)=g\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]; \tag{4.1}$$

g is identical with the quantity 4ϵ in de Boer's paper, and σ is the scale factor introduced in Eq. (2.27). The constants ϵ and σ were assumed to have the same values as used by de Boer, namely $\epsilon=1.41\times10^{-15}$ erg and $\sigma=2.561\times10^{-8}$ cm. This potential was substituted into Eq. (2.32), the integrand tabulated as a function of x for various values of τ, and the integration performed numerically. The results are shown in Fig. 1, curve C, while curve A represents the experimental results.[19] The value of r_0 was chosen so that the specific heat had the correct experimental value at the lambda temperature. With a value of $r_0=1.09\times10^{-8}$ cm there is remarkably close agreement, below the lambda temperature, between the theoretical and experimental results. Moreover, this value of r_0 is in good agreement with the value of 1.1×10^{-8} cm obtained from kinetic theory. However, at the lambda temperature itself the discontinuity, calculated from Eq. (2.34), has the wrong sign and is very large ($\sim5R$). The gradient of the specific heat on the high temperature side of the lambda point has also been computed and is found to be very small and negative ($\sim-1R$). Thus, the theoretical behavior at T_λ is in complete disagreement with experiment. This is perhaps disturbing in view of the excellent agreement below the lambda temperature. With the value of r_0 that we have chosen, the specific heat becomes negative for $\tau<0.3$. This clearly indicates that the approximations we have made are breaking down in this region of temperature. This is not altogether surprising considering the nature of the approximations. It may be mentioned that with a slightly smaller value of r_0 the specific heat would be positive over the whole range.

In view of the marked disagreement with experiment at the lambda temperature, it was thought worthwhile to see if any improvement could be obtained by using a different type of potential. From the numerical calculations it was obvious that merely changing the value of r_0 would not alter the qualitative results obtained with de Boer's potential. It was however clear that if the potential was assumed to have a "repulsive hump" at a distance given by $x=1.6$, then the discontinuity in the specific heat would have the correct sign and the gradient on the high-temperature side of the lambda point would be large and negative. Now a potential of this kind corresponds closely to the potential of the *mean* force between helium atoms. Furthermore, by using this type of potential we are taking into account more accurately the fluctuations in density of the number of atoms in the neighborhood of any particular atom. Thus, although the introduction of this potential is somewhat arbitrary, it is not unreasonable on physical grounds.

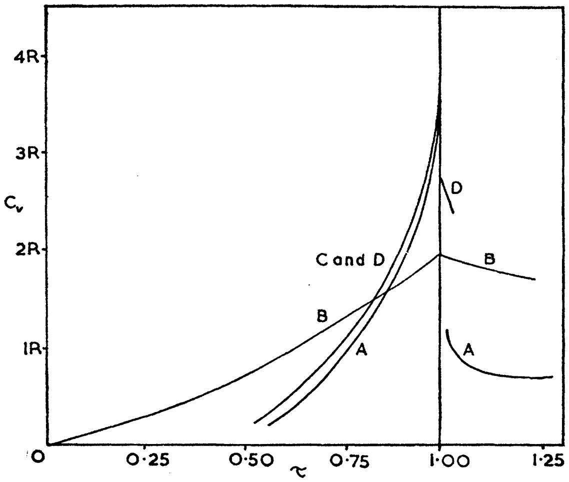

FIG. 1. The specific heat of liquid helium. A—experimental values; B—London theory; C—theory of this paper using de Boer's potential [Eq. (4.1)] for the interaction between the helium atoms; D—this paper using approximate potential of the mean force.

It was not considered worthwhile to attempt to represent this type of potential in any great analytical detail and then perform a numerical integration to obtain the specific heat. It was assumed that for our purpose a sufficiently good representation of it could be obtained by simply changing the sign in de Boer's potential at a distance given by $x=1.6$. The main defect of this potential is that it does not go to zero for large x as $-x^{-6}$, but as $+x^{-6}$. However, the contribution to the integrand is very small at these values of x and this defect will therefore not be very important. The results obtained with this potential are shown in Fig. 1, curve D. To obtain the correct value for the specific heat at T_λ, it was necessary to change r_0 slightly to a value of 1.11×10^{-8} cm. It is seen that below the lambda temperature the curve is indistinguishable from that obtained with De Boer's potential. At the lambda temperature the discontinuity in the specific heat has the correct sign, while the specific heat itself falls off rapidly above the lambda temperature. The break in the specific heat is, however, too small. It seems almost certain that with a sufficiently refined "mean force potential" the behavior

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[19] W. H. Keesom and A. P. Keesom, Physica 2, 557 (1935).

at the lambda temperature could be still further improved. Such calculations are hardly justified when it is remembered that the lambda temperature itself is not correctly predicted by the theory.

In conclusion it is worthwhile considering whether the present treatment exhibits any sort of gas-liquid condensation phenomenon. This question is obviously important, because if it could be shown that the present treatment does in fact exhibit a gas-liquid type of transition then this would lend considerable support to the simple ideal gas theory of London. Unfortunately, there appears to be no simple method of answering this question. The most straightforward method would seem to be to plot a number of isotherms and see if they show any signs of "critical behavior." This would involve a very large amount of numerical work which has not, as yet, been carried out. It is, however, doubtful whether the present method would exhibit any really realistic gas-liquid transition. This is because only two terms in the expansion F have been calculated (approximately); it is very likely that many more terms in the expansion would have to be calculated before a realistic transition occurred.

The numerical work in this section was first carried out on a desk machine. It was subsequently checked by Dr. M. P. Barnett on a punched card machine, using techniques previously developed[20] for the evaluation of molecular integrals. The author wishes to thank Dr. Barnett for the care with which these calculations were carried out. He also wishes to thank Mr. F. Booth for considerable help in the preparation of the manuscript. The author is indebed to the Central Research Fund of London University for the loan of a Marchant calculating machine, and to the Department of Scientific and Industrial Research for a maintenance grant.

APPENDIX

The statistical parameter, α, is defined as a function of ρ and T (that is as a function of T/T_λ) by the equation,

$$N=\sum_{\mathrm{k}}\bar{n}_{\mathrm{k}}(\alpha). \tag{A.1}$$

In the continuous spectrum approximation, this becomes

$$N=(\pi/\lambda)^{\frac{3}{2}}V\sum_{n=1}^{\infty} e^{-n\alpha}n^{-\frac{3}{2}}, \tag{A.2}$$

where $\lambda=h^2/2mkT$. Equation (A.2) holds for $T>T_\lambda$; for $T=T_\lambda$, $\alpha=0$, and Eq. (A.2) becomes

$$N=(\pi/\lambda_0)^{\frac{3}{2}}V\zeta(\tfrac{3}{2}), \tag{A.3}$$

where $\zeta(\frac{3}{2})$ is the Riemann zeta function of order $\frac{3}{2}$, and $\lambda_0=(\lambda)_{T=T_\lambda}$. Dividing Eq. (A.2) by (A.3),

$$\zeta\tau^{-\frac{3}{2}}=\sum_{n=1}^{\infty} e^{-n\alpha}\cdot n^{-\frac{3}{2}}. \tag{A.4}$$

From Eq. (A.4) the derivatives of α may be calculated by direct differentiation. The calculations are made very much easier if the formula given by Robinson[21] is used. He obtains an expansion for $\sum_n e^{-n\alpha}n^{-\mu}$ of the form

$$\sum_{n=1}^{\infty} e^{-n\alpha}n^{-\mu}=\Gamma(1-\mu)\alpha^{\mu-1}+\sum_{p=0}^{\infty}\frac{(-1)^p}{p!}\alpha^p\zeta(\mu-p), \tag{A.5}$$

where $\zeta(\mu-p)$ is the Riemann zeta function of order $\mu-p$, and $\Gamma(1-\mu)$ is the gamma function of argument $1-\mu$. This expansion is valid for $|\alpha|\leq 2\pi$, and all μ. It is easily shown, using (A.5) and (A.4) that for small α $(T>T_\lambda)$,

$$\frac{\partial\alpha}{\partial T}=-\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\zeta(\tfrac{3}{2})\frac{3}{2T_0}\tau^{-5/2}. \tag{A.6}$$

Thus $\partial\alpha/\partial T\rightarrow 0$ as $\alpha\rightarrow 0$. Moreover, as $\partial^n\alpha/\partial T^n\equiv 0 (n\geq 1)$ for $T<T_\lambda$, it follows that $\partial\alpha/\partial T$ is continuous at $T=T_\lambda$. In a similar manner,

$$(\partial^2\alpha/\partial T^2)_{T=T_\lambda}=9[\zeta(\tfrac{3}{2})]^2/8\pi T_\lambda^2, \tag{A.7}$$

showing that $\partial^2\alpha/\partial T^2$ is discontinuous at $T=T_\lambda$. From Eq. (A.4) the following results can be easily deduced:

$$\zeta(\tfrac{3}{2})\frac{3}{2T_\lambda}=\lim_{\alpha\rightarrow 0}\sum_{n=1}^{\infty} e^{-n\alpha}n^{-\frac{1}{2}}\frac{\partial\alpha}{\partial T}, \tag{A.8}$$

and

$$\frac{3}{4}\frac{\zeta(\frac{3}{2})}{T_\lambda^2}=\lim_{\alpha\rightarrow 0}\left[\sum_{n=1}^{\infty} e^{-n\alpha}n^{\frac{1}{2}}\left(\frac{\partial\alpha}{\partial T}\right)^2-\sum_{n=1}^{\infty} e^{-n\alpha}n^{-\frac{1}{2}}\frac{\partial^2\alpha}{\partial T^2}\right]. \tag{A.9}$$

These relations have been used repeatedly in the text.

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[20] M. P. Barnett and C. A. Coulson (to be published).

[21] J. E. Robinson, Phys. Rev. **83**, 678 (1951).