Lambda Transition of Liquid Helium*

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An approximate partition function for a system of interacting Bose-Einstein particles is derived, which is nearly the same as the one derived by Feynman, by neglecting the noncommutability of the potential and kinetic energy operators.

Reasons are given for believing that the approximations introduced in deriving the partition function rather than those introduced in the further development of the partition function are responsible for the difference between the observed and the predicted order of the transition.

1. INTRODUCTION

THE strange behavior of liquid helium,[1] especially its lambda transition and its properties below the lambda point, has been the subject of many theoretical investigations, partly of a phenomenological nature, and partly of a more fundamental nature. Recently, Feynman[2] has approached the problem anew starting from first principles. In F-II and F-III Feynman is mainly concerned with the properties of helium near the absolute zero, or at any rate in the He II region, and we do not wish to discuss that aspect of his theory. In F-I, however, Feynman discusses the partition function of a system of interacting Bose-Einstein particles. Using the space-time approach[3] which he had previously developed for quantum-mechanical problems, Feynman writes down the exact partition function in this case. The further discussion then consists of two steps. The first step is the writing down of an approximate partition function, essentially by considering in detail which trajectories will give the more important contributions to the partition function. The result is given by Eq. (F-I.5). The second step consists of expressing the Helmholtz free energy as a power series in the activity. As Feynman uses petit ensembles, this is done by the method of steepest descents. The coefficients in the power series are then evaluated approximately and it appears that the resultant power series has a singularity corresponding to a third-order transition, using Ehrenfest's classification.[4] In F-I it is suggested that the difference between the predicted order of the transition and the observed second order transition is due to the approximations introduced in the last stage.

In the present paper we wish to show, firstly, how a method developed by Kramers[5] can be used to evaluate the partition function. In Sec. 2 it is shown that to a first approximation this method leads to a partition function which is very similar to the approximate partition function of F-I. The second point we want to discuss is whether the approximate partition function can lead to a transition of the right order. In Sec. 3 we shall give reasons for believing that in going over from the exact to the approximate partition function one has already changed the order of the transition.

2. THE APPROXIMATE PARTITION FUNCTION

We shall use the method of the grand canonical ensembles. We must then evaluate the so-called grand potential q (ESM, p. 137) which is the logarithm of the grand partition function Z and given by the equation (ESM, p. 182)

$$e^q = Z = \text{Trace} \exp(\boldsymbol{n}\nu - \beta \boldsymbol{H}) = \sum_{n=0}^{\infty} e^{n\nu} \text{ Trace} \exp(-\beta \boldsymbol{H}_n), \quad (1)$$

where $\boldsymbol{n}$ is the number operator and $\boldsymbol{H}_n$ the Hamiltonian operator of a system of n particles. The quantity ν is the partial thermal potential (or partial chemical potential) divided by kT (k: Boltzmann's constant; T: absolute temperature), while $\beta = 1/kT$.[6]

One can show (see ESM, pp. 182 to 184) that the right-hand side of (1) can be written as follows:

$$e^q = \sum_{n=0}^{\infty} [e^{n\nu}/n!] \int d^n x \times [\exp(-\beta \boldsymbol{H}_n) \sum_P \prod_i \delta(\mathbf{x}_i - \mathbf{x}_{Pi})]_{\mathbf{x}_{i'} = \mathbf{x}_i}, \quad (2)$$

where $d^n x$ is a short hand notation for the $3n$-dimensional elementary volume $dx_1 dy_1 \cdots dy_n dz_n$, where $\delta(\mathbf{x})$ is the three dimensional delta function, the $\boldsymbol{H}_n$ operate on the $\mathbf{x}_i$ only, where Pi stands for a permutation of the i, where the summation over P is over all possible

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[1] For a comprehensive account see W. H. Keesom, *Helium* (Elsevier Publishing Company, Amsterdam, 1942).

[2] R. P. Feynman, Phys. Rev. **91**, 1291, 1301 (1953); **94**, 262 (1954); hereafter referred to as F-I, F-II, and F-III. See also, G. V. Chester, Phys. Rev. **93**, 1412 (1954); **94**, 246 (1954); hereafter referred to as C-I and C-II.

[3] R. P. Feynman, Revs. Modern Phys. **20**, 367 (1948).

[4] P. Ehrenfest, Proc. Roy. Acad. Sci. (Amsterdam) **36**, 153 (1933).

[5] H. A. Kramers (unpublished). For an account see D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, Inc., New York, 1954), p. 184 ff. (to be referred to as ESM).

[6] In ESM we use μ instead of β.

$n!$ permutations, and where the product is over $i=1$ to n.[7]

Up to this point we have not introduced any approximations. We write now

$$\exp(-\beta \boldsymbol{H}_n)=\exp(-\beta \boldsymbol{U}_n)\cdot\exp(-\beta \boldsymbol{T}_n), \tag{3}$$

where $\boldsymbol{U}_n$ is the potential and $\boldsymbol{T}_n$ the kinetic energy operator of the system,

$$\boldsymbol{U}_n=\sum_{i<j} V_{ij}, \quad \boldsymbol{T}_n=-(\hbar^2/2m)\sum_i \nabla_i^2, \tag{4}$$

where $V_{ij}=V(r_{ij})$ is the potential energy between atoms i and j for which we assume a central force type of potential energy, depending on the distance apart r_{ij}, only, where $\hbar$ is Dirac's constant, where m is the mass of one atom, and where ∇_i^2 is the Laplacian corresponding to the ith atom.

If we use approximation (3) we get, upon using for the delta functions their Fourier integrals (compare ESM, p. 185[8]),

$$e^q=\sum_n (e^\nu/v_0)^n \int d^n x \sum_P \exp(-\beta \sum_{i<j} V_{ij}) \times\exp[-(m/2\hbar^2\beta)\sum_i (\mathbf{x}_i-\mathbf{x}_{Pi})^2], \tag{5}$$

where

$$v_0=(2\pi\beta\hbar^2/m)^{\frac{1}{2}}. \tag{6}$$

Comparing (5) with (F-I.5) we see the following differences. (i) In (5) we have the atomic mass m instead of an effective mass m'. (ii) Instead of an undetermined weight function ρ we have the function $\exp(-\beta\sum V_{ij})$ which has practically the same properties as Feynman's ρ as can easily be ascertained.

Our expression (5) is the same as expression (3) in C-I. This is not surprising as the inclusion of commutators would involve a power series in $\hbar$.[9]

It would be interesting to evaluate the neglected terms. This is in general not a very easy process, but might be possible, if we approximate $V(r)$ by the function

$$V(r)=A,\ 0\leqslant r\leqslant a; \quad V(r)=-B,\ a<r<b; \quad V(r)=0,\ b\leqslant r, \tag{7}$$

or even

$$V(r)=A,\ 0\leqslant r\leqslant a; \quad V(r)=0,\ a<r. \tag{8}$$

The first potential is one with a hard core followed by an attractive potential well, and the second one, in the limit of $A\to\infty$, is that of hard spheres. From experimental data (see, e.g., ESM, p. 202) it follows that $a\cong 2.6$A, $b\cong 4$A, while $B\cong 10^{-15}$ erg.

In the case of $V(r)$ being given by (7) or (8) the correction terms, which arise through the commutator of $\boldsymbol{T}$ with $\boldsymbol{U}$ will all contain delta functions of the form $\delta(r_{ij}-a)$ and $\delta(r_{ij}-b)$, and their derivatives. One might hope to use a power series expansion in terms of βB. This was done by Chester in C-II with striking success as long as only the first two terms of the expansion were taken along. In view of the fact that near the lambda point βB is of the order of magnitude 3, we do not feel that such an expansion will be very useful for our particular purpose. We hope, however, at a later date to return to the question of the neglected terms.

3. THE TRANSITION

It is well known[10] how one can obtain from (1) a power series in the activity (e^ν) for the grand potential. If we write

$$q=\textstyle\sum_s b_s e^{s\nu}, \tag{9}$$

the asymptotic behavior of the b_s will determine the nature and position of the phase transition, if it exists. Essentially, the coefficients b_n are obtained by integrating certain expressions over a so-called cluster of atoms. Two atoms are said to belong to different clusters, if one cannot get from the one to the other over a chain of atoms such that two neighboring atoms in the chain are never further apart than the range of the interatomic forces or than $v_0^{1/3}$, whichever is the larger.

Feynman's approximations in the second stage of his theory consist in taking into account instead of all interactions between the atoms in the cluster, only those interactions which occur along the sides of a polygon. That is, instead of considering interactions between each atom and the $n-1$ other atoms in the cluster, he only considers interactions between each atom and its two neighbors in the polygon.

We do not think, however, that this will lead to serious mistakes, and in particular, contrary to the opinions expressed in F-I and C-I, we do not feel that the order of the transition has been influenced by these approximations. There are two reasons for this. First of all, from C-II we see that taking correction terms of the kind which we might expect in the present case into account can alter the order of the transition. Secondly, we note that both (5) and the equation of state as derived by Feynman's approximation method from (5) are exact for the case of a perfect Bose-Einstein gas. In this case therefore the neglect of all interactions other than those along the polygons did not alter the order of the transition.

It might be argued that the interatomic forces would (or could) alter this result. However, we are dealing

[7] If we would have been dealing with a system of Fermi-Dirac particles, the terms in the summation over all permutations would be multiplied with a factor δ_P which is $+1$ for even and -1 for odd permutations. One can easily introduce this factor δ_P in all subsequent equations and thus obtain the partition function for a system of interacting Fermi-Dirac particles.

[8] There are a few misprints on p. 185 of ESM in the section giving the derivation of Eq. (ESM 8.421); the minus signs in the expression $\exp[-\mu(\hbar^2/2m)\nabla^2]$ should not be there.

[9] One has to be slightly careful, as in the limit $\hbar\to 0$ the only term in the summation over all permutations which will be left is the one with the identical permutation; one can therefore not say that (5) is the classical limit of the partition function.

[10] See, e.g., ESM, Chapter VIII and IX.

with a quantum-mechanical system and the range of the quantum-mechanical diffraction effects—which is essentially $v_0^{1/3}$—is as important as the range of the interatomic forces, as at temperatures of the order of the lambda point $v_0^{1/3}$ is about 3.4A. This means that even though we are dealing with a perfect gas, nevertheless there is an interaction sphere around each atom, and its radius is actually larger than that of the classical helium atom. Any influence from the neglected configurations should thus, in our opinion, show up also in the case of the perfect Bose-Einstein gas.

There is another disturbing fact concerning the partition function (F-I.5) or (5). These expressions should be valid for the gas phase of helium, as the approximation (3) should be least inaccurate at high temperatures and low densities. That means that on lowering the temperature the partition function should reveal the gas-liquid transition before the lambda transition, but this does not happen in the case of (F-I.5) or (5) (compare also the remarks at the end of C-II). This becomes understandable, if we remind ourselves that essentially the attractive forces are neglected in deriving (F-I.5) or (5) (compare the discussion in F-I).

This paper was written while the author was at Purdue University, and I would like to express my thanks to Dr. K. Lark-Horovitz for the hospitality shown to me in his department. In conclusion, I would like to express my gratitude to Dr. R. P. Feynman for pointing out to me some serious mistakes in the first draft of this paper and for making it plausible to me that my original belief that (5) would be exact in the case of hard spheres may not be correct.

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Microwave Determination of the Probability of Collision of Electrons in Helium*

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A previously reported microwave method for determining the collision probability for momentum transfer of slow electrons has been modified so that a variation in average electron energy from 0.012 ev to 3 ev may be obtained. Measurements of the ratio of the real part to the imaginary part of the electron conductivity are performed in the afterglow of a pulsed helium discharge in a microwave resonant cavity. The average electron energy is varied by applying a microwave electric field in the afterglow and, under appropriate assumptions, the average electron energy is determined theoretically from this field. Measurements are also obtained by varying the gas temperature from 77°K to 700°K. The value of the collision probability for momentum transfer in helium is 18.3±2 percent cm²/cm³ per mm Hg from 0 to 0.75 electron volts and increases slowly to a peak value of 19.2±2 percent at 2.2 ev.

IN a recent paper by Phelps, Fundingsland, and Brown,[1] a microwave method was described for determining the probability of collision for momentum transfer by measuring the conductivity of a decaying plasma after the electrons reach thermal equilibrium with the gas. The method has been modified so that a variation in average electron energy from 0.012 to 3 electron volts was obtained. The electron conductivity in the afterglow was studied as a function of experimental parameters and the effects of electron energy, impurities in the gas, ambipolar diffusion, nonuniform electric heating fields, and energy gradients were investigated. The experimental conditions were such that the electron energy distribution function was known. This enabled an expression for the probability of collision for momentum transfer as a function of electron energy to be determined from the experimental data.

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[1] Phelps, Fundingsland, and Brown, Phys. Rev. 84, 559 (1951).

ELECTRON CONDUCTIVITY RATIO IN THE AFTERGLOW

Margenau[2] has given a general theory for the behavior of electrons in a gas under the action of a high-frequency field when only elastic collisions need be considered. From his results the complex electron conductivity σ_c may be written as:

$$\sigma_c=\sigma_r+j\sigma_i=-\frac{4\pi}{3}\frac{ne^2}{m\omega}\int_0^\infty \frac{[(\nu_m/\omega)-j]}{1+(\nu_m/\omega)^2}v^3\frac{df_0}{dv}dv. \quad (1)$$

Here n is the electron density, e and m are the electronic charge and mass, ω is the radian frequency of the applied field, f_0 is the first term in the spherical harmonic expansion of the normalized electron velocity distribution function for electrons of velocity v. The collision frequency for momentum transfer ν_m is related to the probability of collision for momentum transfer, P_m, by $\nu_m=P_m p_0 v$, where p_0 is the pressure normalized to zero degrees centigrade.

[2] H. Margenau, Phys. Rev. 69, 508 (1946).