Quantum-Statistical Theory of Liquid Helium

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(Received August 4, 1951)

The lambda transition in liquid helium is investigated on the basis of quantum statistical mechanics. In the first place, the partition function for an assembly of Bose particles is formulated in such a way that the effect of Bose statistics appears as a strong attractive potential between particles and gives rise to molecular clustering of various sizes, so that the assembly can be considered as a system of molecules and atoms obeying Boltzmann statistics. This formulation is then applied to the ideal Bose gas and to the actual helium liquid, and the following results are obtained: (a) An ideal Bose gas undergoes a phase transition similar in its formal property to the condensation of a classical imperfect gas. (b) By taking into account the interatomic potential, but neglecting all the quantum effects but the statistics, we obtain a jump in the specific heat curve at the transition temperature and a value of the transition temperature coming nearer to the actuality. (c) Beside the molecular clustering, or the “Bose-excitation,” the quantum effects bring in the “Debye phonons” and the “Landau rotons,” the former corresponding to the translational motions of the molecules and the atoms, and the latter to the rotational motions of the molecules. Although the quantum effects are not dealt with in detail, the agreement between theory and experiments is shown to be improved by taking them into account. It is also shown that these effects probably are not of very great importance even near the lambda point.

§ 1. Introduction

The peculiar properties of liquid helium II have hitherto been well explained by phenomenological theories based on two-fluid model, although the molecular-theoretical interpretation of the model itself still remains almost unsolved. Two well-known theories, one due to London and Tisza and the other due to Landau, have so far appeared in competition, and some of the behaviours of helium II stand in favour of the former but others are more favourable to the latter. Experiments on mixtures of He and He or on pure He show that He does not take part in superfluidity and this gives a support to the London-Tisza theory which starts from the concept of Bose-Einstein condensation, while Landau’s theory is incapable of explaining this fact. On the other hand, experiments on the temperature and pressure dependencies of second sound velocity rather support the predictions from Landau’s theory, while some theories developed recently along the line of London-Tisza’s idea do not seem successful in explaining its behaviours near absolute zero. These circumstances indicate the imperfectness of both theories, and one will be lead to scrutinize their foundations.

Confining ourselves to the properties of liquid helium in thermal equilibrium,
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as we shall do in this paper, the following points must thus be expected to result from a correct theory:

a) Helium remains to be liquid at absolute zero because of the light mass of the atom and a weak interatomic force.

b) A phase change occurs at a certain temperature on account of the Bose-Einstein statistics for He^4; the lower phase possesses a peculiar character of allowing for the existence of two velocity fields.

c) There exists in the lower phase a quantity which characterizes its internal structure, for instance a parameter \( x \) that defines the mixing ratio of the two velocity fields.

We attempt in the present paper to develop a theory of liquid helium on the basis of orthodox quantum-statistical mechanics, with a hope to obtain some clues to the real solution, and we believe that an answer to some of the points cited above is really given by our treatment. We first develop a general method suitable for analyzing the effect of Bose-Einstein statistics for a system composed of a large number of particles (§ 2). This method is then applied to an ideal gas, where we show that we can interpret the Bose-Einstein condensation in terms of space coordinates alone (§ 3). This application provides us a ground to go a step further and treat a system of interacting particles. We first neglect all the quantum-mechanical effects except for the statistics in treating a system of interacting particles, and show that the behaviours of the phase transition comes nearer to actuality by inclusion of the interatomic forces (§ 4). Finally, the quantum effects are taken into consideration, though not perfectly (§ 5). We show there that these effects do not influence essentially the behaviours of the phase transition, but that they rather provide us some possibilities of accounting for the anomalous behaviours found at lower temperatures.

§ 2. General quantum-statistical mechanics of an assembly of Bose particles

Let the Hamiltonian of a system of \( N \) Bose particles be \( H \). Then we have the density matrix of the system in coordinate representation in the form

\[
\rho_N(r_1...r_N; r'_1...r'_N) = \sum_k \psi_k^*(r'_1...r'_N) e^{-\beta H} \psi_k(r_1...r_N),
\] (2.1)

where the wave functions \( \{\psi_k(r_1...r_N)\} \) are an arbitrary set of orthogonal normalized functions symmetric with respect to the coordinates. For instance, we may construct them from a set of orthogonal normalized functions of one coordinate, \( \phi_1(r), \phi_2(r), \phi_3(r), \ldots \), in the following way:

\[
\psi_{n_1n_2...}(x) = \frac{1}{\sqrt{N! \prod n_i !}} \prod_{\sigma} \sum \mathcal{P} \psi_{n_1n_2...}(x),
\] (2.2)
where we mean by \( \Psi_{n_1 n_2 \ldots}(x) \) a product of \( n_1 \phi_1, n_2 \phi_2, \ldots (n_1+n_2+\ldots=N) \) with \((r_1, r_2, \ldots, r_N) = x\) arranged in their order, that is,

\[
\Psi_{n_1 n_2 \ldots}(x) = \phi_1(r_1)\phi_2(r_2) \ldots \phi_n(r_n) \phi_{n_1+1}(r_{n_1+1}) \ldots
\]

and by \( P \) a permutation operated upon the coordinates, the summation being extended over all the permutations. Substituting (2.2) in (2.1) and taking the trace of the density matrix, we have the sum over states:

\[
Z_N = \frac{1}{N!} \sum_{\{n_k\}} \sum_{P} \frac{1}{n_1! n_2! \ldots} \int \ldots \int P^* \Psi_{n_1 n_2 \ldots}(x) e^{-\beta H} \Psi_{n_1 n_2 \ldots}(x) \, dx
\]

\[
= \frac{1}{N!} \sum_{\{n_k\}} \sum_{P} \frac{1}{n_1! n_2! \ldots} \int \ldots \int P^* \Psi_{n_1 n_2 \ldots}(x) e^{-\beta H} \Psi_{n_1 n_2 \ldots}(x) \, dx. \quad (2.3)
\]

This expression can be written in another way. We may namely start from another set of functions which we obtain from \( \Psi_{n_1 n_2 \ldots}(x) \) by changing the order of arrangement of the \( \phi \)'s in the product through a definite permutation. Evidently we then have the same result. Since there are just \( N!/n_1! n_2! \ldots \) essentially different such permutations for a given set \( n_1, n_2, \ldots \), (2.3) can be written as

\[
Z_N = \frac{1}{N!} \sum_{P} \sum_{k} \int \ldots \int P^* \Psi_{k}(x) e^{-\beta H} \Psi_{k}(x) \, dx, \quad (2.4)
\]

if we imply by \( \{ \Psi_{k}(x) \} \) the complete set of functions \( \{ \phi_{k_1}(r_1)\phi_{k_2}(r_2) \ldots \phi_{k_N}(r_N) \} \) with \( k_i=1, 2, 3, \ldots \) \((i=1, 2, \ldots, N)\). Furthermore, we have the same value of the sum behind \( \sum \) in the above expression when \( P \) runs over every element of the same class of the symmetric group \( S_N \). To see it, we take a set \( k_1', k_2', \ldots, k_N' \) which we obtain from \( k_1, k_2, \ldots, k_N \) by changing the order of arrangement of the latter through a permutation \( T \). It merely means a change of order of the summation over \( k \). But this permutation is equivalent to replacing the integrand by

\[
PT^{-1} \Psi_{k}^*(x) e^{-\beta H} T^{-1} \Psi_{k}(x)
\]

whose integral is equal to

\[
\int \ldots \int TPT^{-1} \Psi_{k}^*(x) e^{-\beta H} \Psi_{k}(x) \, dx
\]

as one sees by the change of variables \( Tx = x' \).

Therefore, the summation over \( P \) can be substituted by a sum over the classes of the symmetric group \( S_N \), namely,
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\[ Z_N = \sum_{\{m_i\}} \frac{N!}{\prod_{i=1}^{N} m_i \cdot \prod_{i=1}^{N} m_i} Z(m_1, m_2, \ldots, m_N) / N!, \quad (2.5) \]

\[ h_{m_1, m_2, \ldots, m_N} = \frac{N!}{\prod_{i=1}^{N} m_i \cdot l_{m_i}}, \quad (2.6) \]

\[ Z(m_1, m_2, \ldots, m_N) = \sum_{k} \int \cdots \int P \Psi_k^*(x) e^{-\beta H} \Psi_k(x) \, dx, \quad (2.7) \]

\( P \) = any element of the class \((m_1, m_2, \ldots, m_N)\).

Here (2.6) is the number of elements in the class characterized by \( m_1, m_2, \ldots, m_N \), where \( m_1 \) is the number of cycles of length 1 in the permutation, \( m_2 \) that of length 2, and so on, so that \( \sum_l m_l = N \).

The expression here obtained is especially suited for investigating the effect of the statistics upon the thermal properties of the assembly because \( \Psi_k(x) \)'s are not the symmetrized functions. Indeed, the term which corresponds to the identical permutation,

\[ \frac{1}{N!} Z(N, 0, \ldots, 0) = \frac{1}{N!} \sum_{k} \int \cdots \int \Psi_k(x) e^{-\beta H} \Psi_k(x) \, dx, \quad (2.8) \]

is nothing but the sum over states (divided by \( N! \)) for an assembly of particles which obey Boltzmann statistics, and should be expected to be dominant at high temperatures, while other terms represent corrections due to Bose statistics. In the next section, we shall see by applying (2.5) to the case of ideal gas that our division into the classes of \( S_N \) bears a close relationship to the Bose condensation. Moreover, since the present formalism is quite general, it is possible to extend our computations to the case of interacting particles, and at the same time to criticize how far reaching is the application of the ideal gas model to liquid helium.

§ 3. The condensation of ideal Bose gas

In the case of an ideal gas, the Hamiltonian is a sum of commuting operators:

\[ H = \frac{1}{2m} \sum_{i=1}^{N} p_i^2. \quad (3.1) \]

In such a case, we can obtain the sum over states in a compact way, and indeed exactly in the case of an ideal gas. Writing the density matrix of one particle as

\[ \rho (\mathbf{r} ; \mathbf{r}' | \beta) = \sum_{k} \phi_k^* (\mathbf{r}') e^{-\beta p^2 / 2m} \phi_k (\mathbf{r}), \quad (3.2) \]

we have straightforwardly
$Z(m_1, m_2, ..., m_N) = \prod_{i=1}^{N} (I_i)^{m_i}$,  \hspace{1cm} (3.3a)

$I_i = \int \cdots \int \rho(r_1, r_2 | \beta) \rho(r_2, r_3 | \beta) \cdots \rho(r_{i-1}, r_i | \beta) \, dr_1 \cdots dr_i$

$= \int \rho(r | l\beta) \, dr$  \hspace{1cm} (3.3b)

($l\beta = l$ times $\beta$). Now we define "cluster integrals $b_l$" by

$I_i = V l b_i. \quad (V = \text{volume of the assembly})$  \hspace{1cm} (3.4)

Then we have

$$Z_N = \sum_{m_1}^{N} \prod_{i=1}^{N} \frac{(V b_i)^{m_i}}{m_i!} \sum_{l m_1 = N}^{l = 1}$$

which is the familiar form obtained in the case of a classical imperfect gas.  \hspace{1cm} (3.5)

Taking plane waves for $\psi_{k}(r)$'s, we obtain after a simple calculation the following expression of $b_i$ for sufficiently large volume $V$:

$$b_i = \left\{ \begin{array}{ll}
 1 & i \neq 1 \\
 \frac{1}{V^{1/2}} \frac{1}{(\mu_1 !)^2} b_0 \frac{1}{V} + \frac{1}{V} \frac{1}{V} \end{array} \right\}$$  \hspace{1cm} (3.6)

The term $1/IV$ is contributed from the state of zero momentum; it is negligible at high temperatures or for large volume, but becomes important when condensation begins. Inserting (3.6) into (3.5), we have

$$Z_N = \sum_{N_0=0}^{N} \left[ \sum_{\{m_1\}} \sum_{\{\mu_1\}} \left\{ \prod_{i=1}^{N} \frac{(V b_0)^{m_i}}{m_i!} \prod_{i=1}^{N} \frac{1}{\mu_i ! \mu_1 !} \right\} \right]$$  \hspace{1cm} (3.7)

$$= \sum_{N_0=0}^{N} \left\{ \sum_{\{m_1\}} \prod_{i=1}^{N-N_0} \frac{(V b_0)^{m_i}}{m_i!} \right\} \left( \cdots \sum_{\{\mu_1\}} \prod_{i=1}^{N} \frac{1}{\mu_i ! \mu_1 !} = 1 \right)$$ \hspace{1cm} (3.7')

Obviously $N_0$ is the number of particles in the lowest state of zero momentum. We now adopt the approximation of replacing $\log Z_N$ by the logarithm of the maximum term of the right-hand side of (3.7'). The logarithm of the maximum term for a given $N_0$ is

$$\log Z(N_0) = (N - N_0) a + V \sum_{i} \int \, b_i \, e^{-i a},$$ \hspace{1cm} (3.8)

where $a$ is determined from

$$V \sum_{i} \, b_i \, e^{-i a} = N - N_0.$$ \hspace{1cm} (3.9)
Next, differentiating \( \log Z(N_0) \) with respect to \( N_0 \), we have \( a=0 \). Putting \( a=0 \) in (3.9), we have the equation which determines \( N_0 \):

\[
V \left( \frac{2\pi mk T}{h^2} \right)^{3/2} \sum_{\ell=0}^{\infty} \frac{1}{\ell^{3/2}} = N - N_0 .
\]

(3.10)

Since, however, \( N_0 \) cannot be negative, \( a=0 \) is not allowed for temperatures higher than \( T_0 \) determined by

\[
V \left( \frac{2\pi mk T_0}{h^2} \right)^{3/2} \sum_{\ell=0}^{\infty} \frac{1}{\ell^{3/2}} = N .
\]

(3.11)

For such temperatures \( N_0=0, a>0, \) and \( a \) is determined by

\[
V \left( \frac{2\pi mk T}{h^2} \right)^{3/2} \sum_{\ell=0}^{\infty} \frac{e^{-2\ell}}{\ell^{3/2}} = N .
\]

(3.12)

Therefore, we have two phases below and above \( T_0 \):

\[
T < T_0 : \quad N_0 \neq 0, \quad a = 0 ,
\]

\[
T > T_0 : \quad N_0 = 0, \quad a > 0 .
\]

(3.13)

This is the well-known Bose condensation. We shall show in the next section that the method of derivation here presented can be followed almost without modification in the case of interacting particles.

\section{4. Theory of the Bose liquid, taking into account only the effect of the statistics}

As the first step to the study of the influence of interatomic forces on the condensation, we shall neglect all the quantum-mechanical effects except for the statistics. Such a treatment is interesting because it provides us an insight to see whether the Bose statistics is essential for the phase transition in liquid helium or not. Indeed, we shall see below that the knick in the specific heat curve in the case of an ideal gas changes to a discontinuity by inclusion of the interatomic forces.

The neglect of the quantum effect is equivalent to treating the momentum operators to commute with the potential energy. We take the Hamiltonian as

\[
H = \frac{1}{2m} \sum_{s=1}^{X} \mathbf{p}_s^2 + \sum_{s \neq t} \varphi(r_{st}) = \frac{1}{2m} \sum_s \mathbf{p}_s^2 + \Phi(r_1 \ldots r_X) ,
\]

(4.1)

where \( \varphi(r_{st}) \) is the potential energy between the particles \( s \) and \( t \). Taking for \( \{ \mathcal{F}_k(\alpha) \} \) again the set of plane waves...
the sum over $k$ is replaced approximately by an integral over $p_1 \ldots p_N$:

$$
\sum_k \rightarrow \frac{V}{\hbar^3} \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} dp_1 \ldots dp_N,
$$

and (2.5) becomes

$$
(4.3)
$$

with

$$
(4.4)
$$

where we understand by $s'$ the index of coordinate which we have from $s$ through a permutation $P$ in the class $(m_1 \ldots m_N)$. Thus, $m_1$ terms in $\sum_{l=1}^{N-1} (r_s - r_{s'})^2$ vanish, $m_2$ pairs of terms appear in closed form like $r_{12}^2 + r_{34}^2$, $m_3$ sets of three terms appear in closed form like $r_{56}^2 + r_{78}^2 + r_{910}^2$, and so on. The permutation $P$ introduces, therefore, an apparent potential energy of the form

$$
(4.5)
$$

and this gives a tendency for $m_l$ sets of $l$ atoms to form $m_l$ "molecules," with $l=2, 3, \ldots, N$.

We now introduce an interatomic potential of the form

$$
\varphi(r) = \epsilon \left( \left( \frac{a}{r} \right)^6 - 2 \left( \frac{a}{r} \right)^4 \right). \quad (4.6)
$$

Then the apparent potential for a pair of atoms which are contained in a molecule is

$$
\Phi = \epsilon \left( \left( \frac{a}{r} \right)^6 - 2 \left( \frac{a}{r} \right)^4 \right) + \frac{\pi}{k^2 \beta} r^2. \quad (4.7)
$$

$\varphi(r)$ depends on temperature. The parameters $\epsilon$ and $a$ will be chosen as

$$
\epsilon = 0.827 \times 10^{-15} \text{ erg}, \quad a = 2.95 \times 10^{-8} \text{ cm}. \quad (4.8)
$$

($m=6.64 \times 10^{-24}$ gr.) The corresponding curve of $\Phi$ for $T=2.19^\circ \text{K} = T_\lambda$ is shown in Fig. 1.
It will be seen that the minimum of $\phi(r)$ is very steep, and is even steeper for higher temperatures. We may expand $\phi(r)$ near its minimum:

$$\beta \phi(r) = \beta \Delta + \frac{r}{2} \left( \frac{r-r_0}{a} \right)^2 + \ldots,$$

(4.9)

with

$$\frac{1}{\sqrt{T}} \approx \left( \frac{\hbar^2}{28\pi a^2} \right)^{3/2} = 0.21 \left( \frac{T_\lambda}{T} \right)^{1/2} \quad (4.10)$$

The breadth of the minimum, $a/\sqrt{T}$, is very small compared with $a$ even for $T_\lambda$; it increases with decreasing temperature.

The analysis given above suggests the following model of the internal structure of liquid helium: each term $Z(m_1 \ldots m_N)$ in $Z_N$ corresponds to an assembly of strongly bonded $m_2$ diatomic molecules, $m_3$ triatomic molecules, and so on, interacting with each other by a weak van der Waals type attraction. Taking the molecular binding energy equal to $\Delta$, as given by (4.9), for an $l$-atomic molecule, we may therefore expect for $Z(m_1 \ldots m_N)$ the following form:

$$Z(m_1 \ldots m_N) \sim \Pi \left( \frac{2\pi M_l kT}{\hbar^2} \right)^{3l/2} e^{-\beta \Delta} \Omega(m_1 \ldots m_N), \quad (4.11)$$

where $M_l$ is the effective mass of an $l$-atomic molecule, $\Omega(m_1 \ldots m_N)$ is the configurational partition function of a liquid consisting of atoms and molecules indicated by $(m_1 \ldots m_N)$. The evaluation of the latter is difficult, although it may be handled with the aid of the theories of multi-component solutions, and we shall not enter into its analysis.

Actually, $Z(m_1 \ldots m_N)$ can be calculated a little more exactly. When carrying out the integration with respect to $l$ coordinates $r_t \ldots r_1$ forming a molecule, we notice that the integrand depends on $r_t \ldots r_1$ very slowly except through the factor

$$e^{-\beta [\phi(r_2) + \phi(r_3) + \ldots + \phi(r_t)]}, \quad (4.12)$$
so that other part than this factor can be put outside the integral. Using the Fourier integral theorem, we have

\[ b_i = \left( \frac{1}{\lambda} \right)^{3/2} \frac{1}{l} \int \left[ e^{-\beta[\phi(r) + \phi(r) + \cdots + \phi(r)]} \right] \, dr, \tag{4.13} \]

where

\[ G(t) = \frac{4\pi}{\lambda^3} \int_0^\infty r^2 e^{-\lambda r^2} \frac{\sin tr}{tr} \, dr. \tag{4.14} \]

Thus \( b_i \) depends no more on \( r_i \). We now use the expansion (4.9) and carry out the integration by the method of steepest descent. Then

\[ G(t) = 2 \left( \frac{2\pi a^2}{r} \right)^{3/2} e^{-2t} \left[ \cos r_0 t + \gamma \left( \frac{r_0}{a} \right) \sin r_0 t \right] e^{-\lambda r^2} , \]

and \( b_i \) can be written in the following form:

\[ b_i = e^{-\lambda \frac{t}{l}} A_i \left( \frac{2\pi M_i kT}{\mu^2} \right)^{3/2} e^{-\lambda \frac{t}{l}} , \tag{4.15} \]

where

\[ \left( \frac{M_i}{m} \right)^{3/2} = A_i = 2 \left( \frac{2\pi a^2}{r} \right)^{3/2} \frac{1}{\sqrt{2}} \int_0^\infty \xi^2 \left[ \cos \sigma \xi + l \sigma \frac{\sin \sigma \xi}{\xi} \right] e^{-\lambda \xi^2} \, d\xi . \tag{4.16} \]

Carrying out such an approximate integration successively for every molecule, we finally arrive at an integral which contain \( m_1 + m_2 + \cdots + m_N \) coordinates, one per each molecule, as integration variables. This integral will be denoted as \( Q(m_1, \ldots, m_N) \) and will not be analyzed further. In any way, we have

\[ Z_N = \sum_{\{m_1, m_2, \ldots\} \in \mathbb{N}} b_1^{m_1} b_2^{m_2} \cdots Q(m_1, \ldots, m_N) , \tag{4.18} \]

The most important result here obtained is that, as the consequence of the Bose statistics, the atoms are excited to form molecules whose energies are higher by \( \Delta \) per atom consisting the molecule than the energy of atoms not forming molecules. It has already been shown by Bijl, de Boer, Michels, and Toda that in such a case we have a strong dependence of entropy on temperature and a discontinuity in the specific heat curve.
To simplify our calculations, we now neglect the interactions between molecules and between molecules and atoms, and we assume a constant mean potential energy \( \varepsilon_0 \) for atoms.

Corresponding with (4·18) the sum over states \( Z_{N-N_0} \) for a given number of zero atoms \( N_0 \) can be written as

\[
Z_{N-N_0} = \sum_{m_1} \frac{(Vb_1)^{m_1}}{m_1!} e^{-\varepsilon_0 m_1},
\]

(4·19)

\[
b_1 = \left( \frac{2\pi m k T}{\hbar^2} \right)^{3/2} e^{-\varepsilon_0},
\]

\[
b_1 = \left( \frac{2\pi M_i k T}{\hbar^2} \right)^{3/2} e^{-\frac{4\Delta}{T^{1/2}}} (I \geq 2),
\]

(4·20)

and the total sum over states is given by

\[
Z_N = \sum_{N_0=0}^{N} Z_{N-N_0}.
\]

(4·21)

As in § 3 we shall adopt the approximation of replacing \( \log Z_N \) by the maximum term of (4·19). For a fixed \( N_0 \) we have

\[
\log Z_{N-N_0} = Nu - N_0 (a + \beta \varepsilon_0) + V \sum_i b_i e^{-\varepsilon_0},
\]

\[
V \sum_i b_i e^{-\varepsilon_0} = N - N_0,
\]

and taking the maximum with respect to \( N_0 \),

\[
ad' = a + \beta \varepsilon_0 = 0,
\]

so that, putting \( \Delta - \varepsilon_0 = \Delta' \), we obtain the following result:

For \( T < T_0 \):

\[
V \left( \frac{2\pi m k T}{\hbar^2} \right)^{3/2} \left\{ 1 + \sum_{l=2}^{\infty} \frac{e^{-\frac{4\Delta'}{T^{1/2}}}}{l^{1/2}} \right\} = N - N_0.
\]

(4·22)

For \( T > T_0 \): \( N_0 = 0 \), and

\[
V \left( \frac{2\pi m k T}{\hbar^2} \right)^{3/2} \left\{ e^{-\varepsilon_0} + \sum_{l=2}^{\infty} \frac{e^{-\frac{4\Delta'}{T^{1/2}}}}{l^{1/2}} \right\} = N.
\]

(4·23)

The transition point is determined from Eq. (4·23) by putting \( a' = 0 \). Formulas for the free energy, the entropy, the specific heat, etc. can be given easily, and they are of the similar forms as those given by Toda, although the calculations in the present case are more complicated owing to the dependencies of \( A_i \) and \( \Delta' \) on temperature. In Fig. 2 and 3 are shown the curves of \( x = (N - N_0)/N \) and of the molar heat as functions of temperature, where we assumed (4·6) and (4·8) for the interatomic potential, the actual volume of liquid helium for \( V/N = v \), and \( -\varepsilon \) for \( \varepsilon_0 \). We obtained the value of the transition temperature as 2.9°K.
a little nearer to the actual transition temperature (2.19°K) than the value given by the ideal gas model (3.14°K). Since our simplification of calculations seems to go too far, we must here be satisfied with a qualitative success of having obtained a discontinuity in the specific heat curve. One of the main obstacles which prevent us from obtaining a quantitative agreement is the temperature variation of $\lambda'$. As may be seen from its definition, $\lambda'$ is nearly proportional to $T^2$ so that $e^{-\lambda' T}$ decreases with increasing temperature, whereas it behaves inversely if $\lambda'$ were a constant. It will be shown in the next section that the quantum effect makes $\lambda'$ tend to a constant value as temperature decreases, and that our quantitative disagreements are removed to some extent by this fact.

To sum up, it is clear that the molecular clustering as the consequence of the Bose statistics, or the "Bose-Einstein excitation," plays a predominant rôle near the lambda point. This clustering is expected to be remarkable down to the temperature where $1/\sqrt{T}$, given by (4.10), reaches 1, that is,

$$0.21\left(\frac{T}{T_e}\right)^{1/2} \sim 1: \quad T \sim 0.96°K.$$  

Although the quantum effect will have an influence on this excitation, we may say that 1°K is the lower limit of the "Bose-Einstein excitation."
§ 5. The quantum effect

It is generally recognized that the quantum effect of helium is already remarkable in gas phase. Uhlenbeck and Beth's calculation,9) for instance, shows that the temperature at which the second virial coefficient of helium gas begins to deviate from its classical value is about 75°K. Accordingly, the neglection of the quantum effect in liquid helium is hardly allowable. One method of taking the quantum effect into consideration is, as often used for gas state, the expansion of the Bloch equation into a power series of $\hbar$. It corresponds to replacing the potential energy of the system, $\Phi(r_1...r_N)$ by

$$\Phi^*(r_1...r_N) = \Phi(r_1...r_N) + \frac{\hbar^2}{24\pi} \left\{ \sum_{i=1}^{N} p_i r_i \cdot \Phi - \frac{1}{2kT} \sum_{i=1}^{N} (p_i \cdot \Phi)^2 \right\} + ... \quad (5.1)$$

when the statistics is not taken into consideration, where $\lambda^2 = \hbar^2 / 2\pi mkT$. For the interatomic potential between two atoms, it thus corresponds to replacing it by

$$\varphi^*(r) = \varphi(r) + \frac{\hbar^2}{12\pi} \left\{ p_1 p_2 \varphi - \frac{1}{2kT} (p_{12} \varphi)^2 \right\} + ... \quad (5.2)$$

Taking the potential (4.6), it proves that these series converges very slowly for the temperature range we are interested in. We therefore cannot use this method. In spite of this, we can get a rough idea of the quantum effect in the present case in the following way. Namely, according to (5.2), this effect causes the minimum of the potential to displace apparently to the side of larger $r$ when the temperature is not too low. Consequently, if one follows the treatment of the preceding section using $\varphi^*(r)$ instead of $\varphi(r)$, $\Delta$ would become greater, and as this effect is more predominant the lower is the temperature, the decrease in $\Delta$ with decreasing temperature is partly cancelled. As mentioned at the end of the last section, this tendency proves to be convenient in explaining the anomalous properties of liquid helium near the lambda point.

It is a very difficult work to develop the quantum mechanics of liquid on the orthodox basis. However, the following method can be adopted for our purpose of the study of the quantum effect on the "Bose-Einstein excitation." Let the sum over states be expressed by (2.5)–(2.7), and the Hamiltonian by (4.1), where the kinetic energy and the potential energy are now non-commutable. In calculating $Z(m_1...m_N)$, we shall classify the coordinates into sets in such a way that those and only those coordinates which are contained in the same set are interchanged by the permutation $P_i$ with an exception that $m_i$ isolated coordinates are gathered into a set. In this way we obtain $1 + m_2 + m_3 + ... + m_N = M$ sets, which we shall enumerate as 1, 2, ..., $M$. Correspondingly, we divide the Hamiltonian into $M$ commutable parts $H_1, H_2, ..., H_M$ which contain each the corresponding coordinates and momenta of the corresponding set, and the potential
energies $V_{ij}$ between different sets ($i \neq j$, $i, j=1, 2, \ldots, M$):

$$H = H_i + H_j + \ldots + H_M + \sum_{ij} V_{ij}.$$  \hspace{1cm} (5.3)

$V_{ij}$ does not commute with $H_i$ and $H_j$ but commutes with the others. If we neglect as the first approximation the non-commutativity of $V_{ij}$ with $H_i$ and $H_j$, we obtain evidently

$$Z(m_1 \ldots m_n) = \prod_{i=1}^n \left( e^{-\frac{\beta}{2} \sum_j V_{ij}} S_i(x_i) \right) \prod_i d x_i,$$  \hspace{1cm} (5.4)

$$S_i(x_i) = \sum_{\Phi} P^i_{\alpha i}(x_i) e^{-\beta H_i \Phi^i_{\alpha i}(x_i)}.$$  \hspace{1cm} (5.5)

Here $\{\Phi^i_{\alpha i}(x_i)\}$ is a complete set for the system of particles contained in the $i$-th set, and $P$ is the identical permutation for the first set of $m_i$ isolated atoms and the cyclic permutation for other sets. Previously, $S_i(x_i)$ ($i \neq 1$) was such a function that has a large contribution to the integral only for those configuration $x_i$ for which the particles in the $i$-th set form a "molecule." We expect this to hold even if the quantum effect is taken into account. A general proof of this expectation is difficult, but we shall show below that it is true in the case of the sets consisting of two particles. If this is allowed, we again arrive at the picture developed in section 4, with an exception that both the internal motions of the molecules and the motions of the molecules and the atoms as the whole are quantized.

We are thus perhaps lead to the conclusion that there are two types of excitation in Bose quantum liquid: one the molecular clustering or the Bose-Einstein excitation which is dominant at higher temperatures, and the other the excitation connected with the quantized thermal motions of the assembly of molecules and atoms, or which may be called "photons" and "rotons," the former prevailing at lower temperatures. This result may be considered as a compromise between Tisza's idea and Landau's. Indeed, the molecules are capable of rotating motion which may correspond to Landau's rotons. However, the two kinds of excitations are not independent of each other, and in case if the coupling among them could be properly treated, one would probably attain a real solution of the problem of the second sound velocity at lower temperatures.

In the last place, we shall study the properties of $S(x)$ for the system of two particles. The Hamiltonian of this system is

$$H' = \frac{1}{2m} p_1^2 + \frac{1}{2m} p_2^2 + \varphi(r), \quad r = |r_1 - r_2|,$$  \hspace{1cm} (5.6)

which can be transformed, by using the coordinates of the center of gravity and the relative coordinate, into the following expression:
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\[ H' = \frac{1}{4m} \left( p_x + p_z \right)^2 + \frac{1}{4m} \left( p_x - p_z \right)^2 + \phi(r) = \frac{1}{4m} \left( p_x + p_z \right)^2 + \mathbf{H}. \] (5.7)

Since we are not interested in the motion of the center of gravity, we set it aside and have

\[ S(r) = \sum_{E, l, m} P\phi_{lm}(Er) e^{-\beta H} \psi_{lm}(Er), \] (5.8)

where

\[ \psi_{lm}(E, r) = \frac{1}{r} \psi_t(E, r) Y_{lm}(\theta, \phi) \] (5.9)

is the eigenfunction of \( \mathbf{H} \) and \( \psi_t(E, r) \) is the solution of the Schrödinger equation

\[ \frac{d^2\psi_t}{dr^2} + \left[ \frac{m}{\hbar^2} (E - \phi(r)) - \frac{l(l+1)}{r^2} \right] \psi_t = 0. \] (5.10)

Neglecting the existence of discrete levels, we normalize \( \psi_t(r) \) in the way

\[ kr \gg 1, \quad \psi_t(kr) \sim \sin(kr + \delta_t(k)), \quad k^2 = \frac{m}{\hbar^2} E, \] (5.11)

and noticing that \( P\psi_{lm}(E, r) = (-1)^l \psi_{lm}(E, r) \), we finally obtain

\[ S(r) = \frac{1}{2\pi^2} \sum_{l=0}^{\infty} (-1)^l (2l+1) \frac{1}{r^2} \int_0^\infty dk \, e^{-\frac{\hbar^2 l^2}{mkr^2}} \psi_t^2(kr) = S_{\text{even}}(r) - S_{\text{odd}}(r). \] (5.12)

\( S_{\text{even}}(r) \) is the sum over even \( l \) and corresponds to the Slater-sum of the system of two Bose particles constructed with symmetric wave functions, and \( S_{\text{odd}}(r) \) is the sum over odd \( l \) and corresponds to the Slater-sum of the system of two Fermi particles. Owing to the normalization condition, \( S_{\text{even}}(r) = S_{\text{odd}}(r) \) for \( r \to \infty \), and \( S(r) \) then vanishes. For small \( r \) both take small values owing to the interatomic repulsion, and it is expected that \( S_{\text{even}}(r) > S_{\text{odd}}(r) \). Accordingly, \( S(r) \) vanishes for \( r \to 0 \) and \( r \to \infty \) and is expected to have a maximum at a certain finite value of \( r \). This maximum should be very sharp at high temperatures but should become broad as temperature is lowered, owing to the quantum effect. If the mean breadth of this maximum is smaller or of the same order as the atomic radius \( a \), it may be allowed to assume that the two particles form a "molecule." To see to what extent this concept of molecular bonding is valid, we shall carry out a computation by use of a rigid sphere model.

* The normalization here adopted is somewhat different from that used in the literature (9). In the case the quantum effect is neglected or there is no interatomic forces, it can be proved that (5.12) is equal to \( S_{\text{class}}(r) \) given by (5.14).

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Take as $\varphi(r)$ the following form:

$$\varphi(r) = \begin{cases} 0 & r > a \\ \infty & r < a \end{cases}. $$

The $v_t(kr)$ satisfying the normalization condition (5.11) is given by

$$v_t(kr) = \sqrt{\frac{\pi kr}{2}} \frac{J_{-1/2}(ka) J_{1/2}(kr) - J_{1/2}(ka) J_{-1/2}(kr)}{\{J_{-1/2}(ka) + J_{1/2}(ka)\}^{1/2}}. \quad (5.13)$$

By use of this function, we can calculate $S(r)$, Eq. (5.12), which we shall denote as $S_{qt}(r)$.

![Fig. 4. Plots of functions $S_{cl}(r)$ and $S_{qt}(r)$ for $T=0.3^\circ K.$](image)

The actual calculation of this quantity is complicated, and we give in Fig. 4 only its value for $r \sim a$ and $r \gg a$ at a very low temperature ($\lambda \gg a$), with $a = 2 \times 10^{-8} \text{ cm}$. The corresponding classical quantity is given by

$$S_{cl}(r) = \frac{V}{\hbar^3} \int_{-\infty}^{\infty} e^{-\beta \varphi(r)} - \frac{\hbar}{m} p^2 + \frac{\hbar}{\ell} (p \cdot r) \, dp = \frac{1}{(2\pi)^{3/2}} e^{-\frac{2\pi \rho^2}{\hbar^2}} e^{-\beta \varphi(r)}, \quad (5.14)$$

and is plotted in the same figure. Although no detail of $S_{qt}(r)$ is obtained from this figure, yet we may say that our expectation is really the case. A measure to indicate to how extent the quantum effect is of importance is provided by the quantity

$$B = \hbar^3 \int_0^\infty 4\pi r^2 [S_{cl}(r) - S_{qt}(r)] \, dr. \quad (5.15)$$
The calculation of this quantity can be executed in the same way as that of the second virial coefficient, and we have

$$B = \frac{k}{\sqrt{2 \pi}} \left[ \sum_{l=0}^{\infty} (-1)^l (2l+1) \Phi_l(s) - \frac{\sqrt{\pi}}{4} \int_0^t e^{-t^2} dt \right]$$

(5.16)

with

$$\Phi_l(s) = \frac{2}{\pi} \int_0^\infty \frac{dx}{x} \frac{e^{-x^2/\tilde{s}}}{F_{1+l/2}(x) + F_{-1+l/2}(x)}, \quad \tilde{s} = \frac{2\pi \sigma^2}{\lambda^2}.$$ (5.17)

Taking the value of $B$ for $s \gg 1$ and $s \ll 1$, and calculating it by interpolation for intermediate values of $s$, we obtain Fig. 5. The temperature at which $B$ is very much different from zero corresponds to $s \sim 1$, or several degrees abs., which is very much lower than the temperature at which the virial coefficient begins to deviate from its classical value, namely, $s \sim 5$. This difference is based on the fact that although the quantum effect appears from very high temperatures for the quantities $S_{\text{even}}(r)$ and $S_{\text{odd}}(r)$, the main part of it cancels by taking their difference, until at very low temperatures. Although we are not sure to have $S_{\text{class}}(r) = S_{\text{even}}(r)$ from $B = 0$, it may fairly well be allowed to conclude that the model developed in section 4 can reasonably be accepted for liquid helium even below the lambda point. Furthermore, the quantity

$$\lambda^3 \int_0^\infty 4\pi r^2 S_{\text{class}}(r) \, dr$$

was computed by use of the method of steepest descent in the preceding section and we had for it $e^{-2\lambda}$. The fact that $B$ increases remarkably at very low temperatures implies the sharp decrease in

$$\lambda^3 \int_0^\infty 4\pi r^2 S_{\text{even}}(r) \, dr = \lambda^3 \int_0^\infty 4\pi r^2 S_{\text{class}}(r) \, dr - B$$

and this in turn implies that, owing to the quantum effect, the quantity $\Delta$ tends to a constant value or even increases with decreasing temperature. From this fact we are lead to expect that a quantitative explanation of the thermal properties of liquid helium is at hand by an extension of our theory more in detail.
§ 6. Conclusion

Our results may be summarized as follows:

(a) There exist two kinds of excitations in a Bose liquid: one the Debye-phonons and Landau-rotons, and the other an excitation corresponding to some molecular clustering, peculiar to an Bose assembly. The latter plays the essential rôle in the phase transition in liquid helium.

(b) As the result of the latter excitation, the Bose liquid has a character of a multi-component solution of associating and dissociating molecules. In the lower modification, there appears a parameter as a thermodynamical variable that describes the equilibrium between these components. Probably the peculiar properties of liquid helium in non-equilibrium would be accounted for by such a character of the system as a multi-component system.

In conclusion, the writer wishes to express his sincere thanks to Prof. T. Nagamiya for his continual interest and helpful advices on the present investigation, and to Dr. R. Kubo for his stimulating discussions during his stay at Tokyo University.

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