A Lattice Model of Liquid Helium, III
—Equilibrium Properties of Liquid He\textsuperscript{4} and Mixtures of He\textsuperscript{4} and He\textsuperscript{3}—

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The partition function of the lattice model of liquid He\textsuperscript{4} developed in the preceding papers\textsuperscript{1,2} is shown to be derived by determining the form of a universal function of one variable so far as one admits three assumptions previously made. Instead of determining the function by using Kikuchi’s approximation as before, the determination is made here by making use of the experimental values of heat capacity at various temperatures under saturated vapour pressure together with two other thermodynamical data at the \textit{kp} point. Comparison of the values thus derived with experimental ones is made for various thermodynamical quantities of pure liquid He\textsuperscript{4} and of mixtures of He\textsuperscript{4} and He\textsuperscript{3}. The agreements are good, and a consistent explanation of various peculiar properties of this liquid is obtained.

§ 1. Introduction

Numerous investigations have been carried out to elucidate the peculiar equilibrium properties of liquid helium from the atomic theoretical point of view. They may be roughly divided into three classes according to the methods of approach. In the first class atoms in the liquid are assumed to be almost free.\textsuperscript{3} The theory fails to include the effect of correlations between the positions of atoms sufficiently. In the second class each atom is assumed to be localized in a cell.\textsuperscript{4} The theory cannot take full account of the quantum-statistical mechanical effect, accordingly of the cooperative character of Bose-Einstein condensation.

Actual He atoms are neither completely localized nor free. Such an intermediary character of atoms in the assembly makes the usual approximation invalid, and yet this character is supposed to be the main origin of the peculiarities of this liquid. The third class, therefore, should be the one which takes account of these circumstances.

Feynman\textsuperscript{5} and Butler-Friedman\textsuperscript{6} independently proposed with some success the theories which may be classified into the third class. Their theories directly start from the well-known exact hamiltonian of the assembly of He atoms and in this sense they are based on the first principles. In turn, however, they are rather complicated and the singular character of this liquid cannot be derived easily from them.

At this stage we may turn our attention to the important roles of the model method in the theory of classical liquid. They served to explain both the equilibrium and non-equilibrium properties of liquids and have brought many a fruitful result. In quantum liquid, too, it would be desirable to have a model, which should belong to the third
class, simple but sufficient to understand the striking features of the liquid.

Along this line of thought Matsubara and Matsuda\(^1\),\(^2\) have developed a lattice model of liquid helium modifying the model previously proposed by S. Koide.\(^7\) (These papers 1) and 2) will hereafter be referred to as I and II respectively.) They carried out approximate calculations taking into account the quantum mechanical and quantum-statistical effects and the effect due to the rigid core of an atom, and succeeded to explain qualitatively some of the peculiar properties of pure He\(^4\) liquid.

In I the lattice model was discussed in terms of a spin system. In order to accomplish the calculation, the molecular field approximation was used. Then the negative thermal expansion coefficient inherent to the substance could not be obtained, while the correct \(\lambda\)-line was obtained by adopting for the mass of the model the true mass of He\(^4\) atom. Further elaboration to the usual Bethe's approximation does not seem to improve this situation.

In II the partition function of the lattice model was directly calculated by counting the number of pertinent closed polygons drawn in the lattice space applying Kikuchi's approximation besides several simplifying assumptions. In this case, although both the correct form of the \(\lambda\)-line and the negative thermal expansion coefficient was obtained, it was necessary to use an effective mass equal to one seventh of the true mass of He\(^4\) atom, which is too small. Moreover, the calculated values of the specific heat are rather small. All these discrepancies are, as we have pointed out in II, supposed to be mainly due to the too rough application of Kikuchi's approximation. Notwithstanding the fact that the restriction imposed on the types of fundamental graphs in II was too severe, the formidable complications will arise if one tries to remove this restriction.

Now, one may notice the fact that in II although the number of fundamental graphs \(g(x_i, y_i)\) involving as its arguments the set of a great many parameters \(x_i, y_i\) fixing the type of F. G.'s, only the value of \(g(x_i, y_i)\) which gives the maximum contribution to the partition function is of predominant importance. This maximum value depends on the independent variables specifying the thermodynamical state of the system (density, temperature and parameters determining hamiltonian of the system). If this dependence is characterized through only few variables which are the functions of the above-mentioned independent variables, we shall have relations between various thermodynamical quantities without knowing all the values of \(g(x_i, y_i)\). Fortunately, in our case, we shall see in the next section that the partition function contains only one universal function of one variable besides the independent variables. It would be worthwhile, then, to determine the universal function empirically and try to understand the relations between various thermodynamical quantities. This is the main technique taken in this paper. We shall see that all salient thermodynamical phenomena in liquid He\(^4\) and in the mixture of liquid He\(^4\) and He\(^3\) are interrelated ones, explicable by a simple physical consideration.

In I and II our discussion was restricted to pure He\(^4\). The basic physical idea was that as the density increases the assembly changes its state from nearly free state to nearly localized one, and the approximation in the first class becomes worse while that in
the second class becomes better. These circumstances, which is absent in the assembly of ideal particles, will be essential to understand the behavior of real He atoms. It will most significantly be reflected on the process involving a change of density. The waves with longer wave lengths essential to the \( \lambda \)-transition are then more and more quenched as the density increases, resulting in the correct density dependence of the \( \lambda \)-line and the possibility of the occurrence of negative thermal expansion coefficient.

This idea will also be applicable when there are He\(^3\) atoms contained as a solute. The peculiar properties of He\(^4\)--He\(^3\) mixture, e.g., large deviation from Raoult’s law, have been discussed phenomenologically by many authors,\(^{10}\) and yet the clear-cut explanation without any ad hoc assumptions does not seem to exist. Making use of analogous considerations as in the case of pure He\(^4\), we shall be able to explain in the later sections the properties of the mixture within the frame of our theory when the concentration of He\(^3\) is low.

In § 2 by the aid of three assumptions introduced in II, various thermodynamical quantities are expressed in terms of a universal function and independent thermodynamical variables. In § 3 the universal function is determined by using the experimental data of heat capacity under saturated vapour pressure and two other data at the \( \lambda \)-point. In § 4 various thermodynamical quantities are calculated by the expressions derived in § 2 and the universal function determined in § 3, and comparison is made between the theory and experiments.

§ 2. Reduction of the various thermodynamical quantities

First we discuss the case of pure He\(^4\) in the same model as in II. We shall here briefly review the considerations and notations in II necessary for discussions in this paper. For detailed accounts the reader is referred to II.

The problem is to calculate the partition function

\[
Z = \text{Trace}\left[\exp(-\beta H)\right],
\]

(1)

where

\[
H = -B \sum_{i,j} a_i^* a_j, \quad B = h^2/2md^2.
\]

(2)

\( a_i^* \) and \( a_i \) are operators which respectively creates and annihilates an atom at the \( i \)-th lattice point. We have seen that expanding \( Z \) as

\[
Z = \text{Trace}\left[\sum_n (-\beta H)^n/n!\right],
\]

(3)

there corresponds to each term of the right-hand side of (3) certain transfer of atoms forming as their trajectories a set of closed polygons in the lattice space. We have classified these sets of closed polygons defining a fundamental graph (F.G.). We have asked, then, in how many ways we can transfer atoms on a F.G. and return to the configuration identical with the initial one after \( 2n \) transfers.

In order to settle the problem we have introduced three assumptions in II. According to Assumption I there are approximately \( [2m \rho_0 \rho_i]^{2n} \) ways of arranging the \( 2n \) transfers,
if we disregard the fact that the final configuration of particles should be identical with the initial one. Here \( \bar{m} \) is the number of lines connecting nearest neighbour lattice points in a skeleton, and \( \rho_0 = (M-N)/M \) and \( \rho_1 = N/M \). \( M \) is the total number of lattice points and \( N \) is the total number of particles. By Assumption II we have to multiply \( [2\bar{m}\rho_0\rho_1]^{2n} \) by \( [s!/\{s\rho_0\/(s\rho_0)\!\}^{-1}] \) in order to correct the number so that the final configuration is identical with the initial one. Here, \( s \) is the number of lattice points forming the skeleton. This corresponds to the assumption that complete randomization of particles has occurred in the F.G. after \( 2n \) transfers independent of the initial configuration.

In order that a graph drawn by arranging \( 2n \) transfers according to Assumptions I and II belongs to the original F.G. with side length \( 2m \), we have to put a further correction factor \( f(m, n) \), which is approximated according to Assumption III by

\[
f(m, n) = \left[\frac{(2n)!}{2^{(n-m)}(n-m)!}\right]^{2m/2n} \rho_0^{2n} \rho_1^{2n} \left[\frac{s!}{\{s\rho_0\!\}^{-1}}\right]^{-1},
\]

for \( n > m \) and \( n-m < m \).

Thus we have obtained

\[
Z = \frac{M!}{(M-N)! N!} \sum_{m} f(m, n) [2\bar{m}\rho_0\rho_1]^{2n} \left(\frac{\beta B}{2n}\right)^{2n} \left[\frac{s!}{\{s\rho_0\!\}^{-1}}\right]^{-1},
\]

where \( S \) means the summation over all possible F.G.’s.

Each F.G. has been classified by a set of parameters \( \{x_i\} \) and \( \{y_i\} \) specifying a type of F.G. Denoting by \( g(\{x_i\}, \{y_i\}) \) the number of F.G.’s belonging to the set of parameters \( \{x_i\} \) and \( \{y_i\} \), we have

\[
Z = \frac{M!}{(M-N)! N!} \sum_{\{x_i\}, \{y_i\}} g(\{x_i\}, \{y_i\}) \sum_{m} f(m, n) [2\bar{m}\rho_0\rho_1]^{2n} \left(\frac{\beta B}{2n}\right)^{2n} \left[\frac{s!}{\{s\rho_0\!\}^{-1}}\right]^{-1}.
\]

We have seen in II that in the vicinity of the 4-point we can approximate as

\[
s \approx 2m \approx 2n \approx 2\bar{m}.
\]

Admitting (7), we obtain from (6) for the logarithm of the partition function per lattice point without making direct use of Kikuchi’s approximation

\[
\bar{P} = \text{Max} \left[ \frac{\ln g(\{x_i\}, \{y_i\})}{M} + \frac{2n(I' + A)}{M} - A \right]
\]

\[
= \text{Max} \left[ \frac{P(\{x_i\}, \{y_i\}, n)}{M} \right],
\]

where

\[
I' = \ln(\rho_0\rho_1\beta B), \quad A = \rho_0 \ln \rho_0 + \rho_1 \ln \rho_1.
\]

The values of \( \{x_i\}, \{y_i\} \) and \( n \) are to be determined so as to make \( P(\{x_i\}, \{y_i\}, n) \)
maximum for given values of $I'$ and $A$. Therefore, $\bar{P}$ can be written as

$$\bar{P} = \varphi(Y) - A,$$

where $\varphi(Y)$ is a universal function dependent solely through $Y$ on the variables specifying the thermodynamical state of the system.

When we deal with the mixtures of He$^4$ and He$^3$, we note that (i) if the concentration of He$^3$ is low the possibility that He$^3$ atoms exchange their positions is very small compared with that of He$^4$ atoms. Therefore, the most part of the contributions to the partition function comes from the graphs in which most He$^3$ atoms return after $2n$ transfers to their own initial points; (ii) even when they happen to exchange their places, due to the Fermi statistics the contribution is negative if the permutation is odd. Both of these two facts will reduce the contribution from transfers of He$^3$ atoms to a considerable extent.

Thus, it will be safe to regard He$^3$ atoms as fixed, so far as the concentration of He$^3$ is not too high and the temperature is not too low. The $2nI'$ in (8) should now be written as

$$2nI' = 2n \ln (\rho_0 \rho_4 \beta B),$$

$$\rho_4 = N_4/M,$$

where $N_4$ is the number of He$^4$ atoms. Corresponding to Assumption II of II, the probability of returning to the initial configuration will here be approximated by the reciprocal number of ways that $s\rho_4$ He$^4$ atoms and $s\rho_0$ holes can be distributed among $s(\rho_0 + \rho_4)$ lattice points, i.e. $[s(\rho_0 + \rho_4) \ldots (s\rho_0) \ldots (s\rho_4)]^{-1}$.**

This requires that the $2nA$ appeared in (8) should be

$$2nA = 2n \{\rho_0 \ln \rho_0 + \rho_4 \ln \rho_4 - (\rho_0 + \rho_4) \ln (\rho_0 + \rho_4)\},$$

and the last term $A$ in (8) should be replaced by

$$\bar{A} = \rho_0 \ln \rho_0 + \rho_4 \ln \rho_4 + \rho_3 \ln \rho_3, \quad \rho_3 = N_3/M$$

respectively, where $N_3$ is the number of He$^3$ atoms.

Summarizing the above we have for the logarithm of the partition function per lattice point

$$\bar{P} = \varphi(Y) - \bar{A},$$

* This consideration applies to the system of liquid He$^4$ containing as dilute solute any foreign atoms. It is then expected that these systems will show similar thermodynamical properties.

** Strictly speaking the immobile He$^3$ atoms will act as an obstacle to the transfer of He$^4$ atoms, contradictory to the fact that the $s$ lattice points belong to a F.G. defined in II. Here, we may think we have roughly taken into account the possibility that He$^3$ atoms evade the He$^4$ atom and return afterwards to their initial positions.
Here $m_i$ is the mass of a He\(^4\) atom.

Free energy $F$, internal energy $E$, entropy $S$, heat capacity at constant volume $C$, and pressure of the system $p$ can easily be written down as

\begin{align*}
F &= -MkTP, \quad \text{(15)} \\
E &= -M(\partial F/\partial Y) (\partial Y/\partial \beta) = -M(\partial \varphi/\partial Y) e^A \rho_0 \rho_4 B, \quad \text{(16)} \\
S &= (E-F)/T = kM(\bar{p} - Y \cdot \partial \varphi/\partial Y), \quad \text{(17)} \\
C &= kMY^2 \cdot \partial^2 \varphi/\partial Y^2, \quad \text{(18)} \\
p &= kT/d^3 \cdot (\bar{p} + M \cdot \partial \bar{p}/\partial M) \\
&= kT/d^3 \left[ \bar{p} + \rho_4 \ln \rho_4 + \rho_3 \ln \rho_3 - \rho_4 \ln \rho_0 + \partial \varphi/\partial Y \cdot Y [\rho_4 \ln \rho_4 - \rho_3 \ln \rho_3 - \rho_4 \ln (1 - \rho_3) + \rho_4/\rho_0 - 1] \right]. \quad \text{(19)}
\end{align*}

At the $\lambda$-point the heat capacity expressed in (18) should have a discontinuity. Since $\varphi(Y)$ is a universal function, the singularity should always occur at the same value of $Y$. The $\lambda$-point is, therefore, determined by

$$
\exp[A + \Gamma'] = Y_\lambda, \quad \text{(20)}
$$

where $Y_\lambda$ is a constant.

So far we have left the effect of attractive forces out of consideration. As the range of attractive force is larger than that of repulsive force we may take as a first approximation that every atom experiences the constant field of attraction so long as it is in the liquid. The potential energy per atom due to attractive force being thus assumed constant, its inclusion does not change the matter in the process where the number of atoms is kept constant as above. In order to obtain the expression for chemical potential, let this mean attractive potential energy per atom be $\bar{\varepsilon}$.

The chemical potential for He\(^4\) in the liquid is then

$$
\mu_4 = (\partial F/\partial N_4) = 1/M \cdot (\partial F/\partial \rho_4) \rho_3
= -kT \left( \frac{\partial \varphi}{\partial Y} - \frac{\partial A}{\partial \rho_4} \right) + \bar{\varepsilon}
= -kT \left[ \frac{\partial \varphi}{\partial Y} \left( \left( \frac{1}{\rho_4} - \frac{1}{\rho_0} \right) + \ln \left( \frac{\rho_4}{\rho_0} \right) \right) - \ln \left( \frac{\rho_4}{\rho_0} \right) \right] + \bar{\varepsilon}, \quad \text{(21)}
$$

and for He\(^3\)
\[ \mu_s = \left( \frac{\partial F}{\partial N_s} \right) x_s = 1/M \cdot \left( \frac{\partial F}{\partial \rho_s} \right) \rho_s \]

\[ = -kT \left[ \frac{\partial \varphi}{\partial Y} \left\{ -\frac{1}{\rho_0} + \ln \left( \frac{1-\rho_3}{\rho_0} \right) + \ln \left( \frac{\rho_3}{\rho_0} \right) \right\} \right] + \varepsilon. \]

(22)

If we assume the vapour of helium as an ideal gas, the chemical potential in the vapour for He\(^4\) and for He\(^3\) are

\[ \tilde{\mu}_4 = kT \left( \ln \tilde{\rho}_4 - \frac{3}{2} \ln \lambda_4 \right), \]

\[ \tilde{\mu}_3 = kT \left( \ln \tilde{\rho}_3 - \frac{3}{2} \ln \lambda_3 \right), \]

(23)

(24)

respectively, where

\[ \lambda_4 = \frac{(2\pi m_4 kT)}{h^2}, \quad \lambda_3 = \frac{(2\pi m_3 kT)}{h^2}. \]

\(\tilde{\rho}_4\) and \(\tilde{\rho}_3\) are the number density of He\(^4\) and He\(^3\) in the vapour, and \(m_4\), \(m_3\) are the mass of a He\(^4\) and He\(^3\) atom respectively.

From the equation

\[ \mu_4 = \tilde{\rho}_4 \quad \text{and} \quad \mu_3 = \tilde{\rho}_3, \]

(25)

we obtain

\[ \tilde{\rho}_4 = \frac{\rho_4}{\rho_0} \exp \left[ -\frac{\partial \varphi}{\partial Y} Y \left\{ -\frac{1}{\rho_4} + \ln \left( \frac{1-\rho_4}{\rho_0} \right) - \ln \left( \frac{\rho_4}{\rho_0} \right) \right\} \right], \]

(26)

\[ \tilde{\rho}_3 = \frac{\rho_3}{\rho_0} \exp \left[ -\frac{\partial \varphi}{\partial Y} Y \left\{ -\frac{1}{\rho_3} + \ln \left( \frac{1-\rho_3}{\rho_0} \right) \right\} \right]. \]

(27)

Hence,

\[ \frac{C_V}{C_L} = \frac{\tilde{\rho}_3/\tilde{\rho}_4}{\rho_3/\rho_4} = \left( \frac{m_3}{m_4} \right)^{3/2} \exp \left[ -\frac{\partial \varphi}{\partial Y} Y \left\{ -\frac{1}{\rho_4} + \ln \left( \frac{1-\rho_4}{1-\rho_3} \right) \right\} \right]. \]

(28)

§ 3. Determination of the universal function \(\varphi(Y)\)

In II we have seen that if we set the lattice spacing \(d=3.1\) \(\text{Å}\), the correct density dependence of \(T_\lambda\) is obtained. Here, we use the same value for \(d\) as before, but use the true mass \(6.69 \times 10^{-24} \text{gr}\) for \(m_4\). From the fact that when \(\mu_4=0.65\), \(\mu_3=0\), the density is about \(0.147 \text{gr/c.c.}\) and the corresponding experimental \(\lambda\)-temperature is about \(2.16^\circ\text{K}\), we obtain

\[ Y_\lambda = \left( e^{A (\rho_4 \rho_3 B)} \right) \lambda \simeq 0.0344. \]

We can get the explicit form of \(\varphi(Y)\) by numerical integration of eq. (18) making use of the experimental value of \(C\) at a fixed density. We employ for simplicity the data of \(C\) under saturated vapour pressure, the density of which approximately corresponds to \(\mu_4=0.65\), \(\mu_3=0\). As eq. (18) is of the second order in the derivative of \(\varphi(Y)\), we have to fix two integration constants from experiments. Using eqs. (17) and (28) and experimental values \(C_V/C_L \simeq 10\) and \(S \simeq 0.36 \text{cal/gr}\) for \(\mu_4=0.65\), \(\mu_3=0\), we obtain at the \(\lambda\)-point
The universal function $\phi(Y)$ thus determined is illustrated in Fig. 1, together with its derivative $d\phi/dY$.

§ 4. Comparison with experiments

We can now obtain values for entropy and $C_P/C_L$ for various temperatures and concentrations using eqs. (17) and (28) and the universal function determined in § 3. These curves are shown in Fig. 2 and Fig. 3. To compare the values of pressure with experiments we have to correct (19) for the effect of attractive force. As the anomaly in isopycnals near the $\lambda$-line is considered to be due to that of the kinetic energy, we have assumed for simplicity that the contribution to the pressure from the attractive potential is independent of temperature.

The isopycnals drawn in Fig. 4 are obtained by adjusting the additive constant due to the attractive potential which may depend on density but is assumed independent of temperature so that the correct value of pressure may be obtained at the $\lambda$-line. These curves are generally in good agreement with experiments. The too slow rise of isopycnals with temperature in the region of He I will be due to ignoring the temperature dependence of the effect of attractive potential.

From eq. (20) the concentration dependence of the
In the limit of zero concentration of He\(^3\), we obtain

\[ -dT_\lambda/dX = T_\lambda (1 + \rho_1 \ln \rho_1). \]  

(30)

The result is tabulated in Table I and is compared with experiments.

Thus we have obtained by use of the lattice model a consistent explanation of peculiar

\(\lambda\)-temperature is obtained. If we put

\[ X = \frac{\rho_3}{\rho_1} \]

we have

\[-dT_\lambda/dX = T_\lambda \{ \frac{Y_0}{\rho_1} e^{\rho_1/\rho_4 \rho_1} [1/\rho_4 + \ln \rho_4 + \ln (1 - \rho_3)] \}. \]

(29)

properties of liquid He\(^4\) and mixtures of He\(^4\)-He\(^3\) with small concentration of He\(^3\), although we are not free from using several assumptions made in II.

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**Fig. 3.** The Distribution Function versus Temperature (Theoretical)

- (IV) \( \rho_4 = 0.60 \), \( \rho_3 = 0.05 \)
- (V) \( \rho_4 = 0.55 \), \( \rho_3 = 0.10 \)

ATM. 30

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**Fig. 4.** Isopycnals of liquid He\(^4\)

- --- Theoretical curve
- ----- Experimental curve

(I) : \( \rho_1 = 0.70 \)

(II) : \( \rho_1 = 0.75 \)

(III) : \( \rho_1 = 0.80 \)
Table I. Density $\rho$ of He, theoretical and experimental $T_\lambda$, and initial slope of the curve of $T_\lambda$ versus $X$.

<table>
<thead>
<tr>
<th>$\rho_1$</th>
<th>$\rho$ (gr/c.c.)</th>
<th>$T_\lambda$ (theor)</th>
<th>$T_\lambda$ (exp)</th>
<th>$\left( \frac{\partial T_\lambda}{\partial X} \right)_{(\text{theor})}$</th>
<th>$\left( \frac{\partial T_\lambda}{\partial X} \right)_{(\text{exp})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>0.147</td>
<td>2.16</td>
<td>2.16</td>
<td>-1.56</td>
<td>-1.5</td>
</tr>
<tr>
<td>0.70</td>
<td>0.158</td>
<td>2.07</td>
<td>2.10</td>
<td>-1.55</td>
<td>-</td>
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<tr>
<td>0.75</td>
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<td>1.94</td>
<td>1.97</td>
<td>-1.52</td>
<td>-</td>
</tr>
<tr>
<td>0.80</td>
<td>0.180</td>
<td>1.76</td>
<td>1.76</td>
<td>-1.44</td>
<td>-</td>
</tr>
</tbody>
</table>

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