Lattice Model for Quantum Liquid Mixtures

Shin TAKAGI

Department of Physics, University of Tokyo, Tokyo

A lattice model is proposed in order to investigate the superfluid phase transition and the phase separation in liquid mixtures of He^3 and He^4. The Matsubara-Matsuda model for pure liquid He^4 is generalized. An effective Hamiltonian is expressed in terms of spin operators with the magnitude unity. It is solved with the aid of molecular field approximation. A phase diagram thus constructed reproduces characteristic features of liquid He^3-He^4 mixtures. Namely, the lambda line, the critical point of the phase separation and the stratification curves are obtained in good agreement with experiments. In addition, it is shown in a unified manner that the lambda temperatures exhibit a qualitatively correct dependence on He^3-concentration and pressure.

§ 1. Introduction

The phase diagram of liquid He^3-He^4 mixtures has been extensively studied experimentally. For a theoretical analysis, it is convenient to divide the phase diagram into two parts, low-temperature and high-temperature regions. At low temperatures near the absolute zero, the Fermi statistics play an essential role. He^3 atoms tend to be distributed uniformly in space in order to reduce their Fermi energy. On the other hand, He^4 atoms prefer to push away He^3 atoms to gain more of the superfluid condensation energy. Thus the Fermi energy competes with the superfluid condensation energy, which leads to an incomplete phase separation even at the absolute zero of temperature.[1] At higher temperatures, below $2.2K$, a superfluid phase transition takes place. The transition temperature, or the lambda temperature, T_λ, decreases with the increasing He^3-concentration x.[2] The lambda line $T_\lambda(x)$ in the T-x plane ends up at a point $(T \simeq 0.87K, x \simeq 0.67)$, where the stratification into two phases begins, namely, into a superfluid phase and a normal phase. It coincides with the critical point (T_c, x_c) of the phase separation.[3] In this high-temperature region, including the critical point, the Fermi statistics may not be so important as in low temperature. In fact an effective Fermi temperature of the mixture with $x = x_c$ is estimated to be so low that it is comparable to the critical temperature T_c.[4] (The effective magnetic Fermi temperature is even much lower as suggested from the data on pure He^3.[5]) He^4 atoms are already degenerate, as manifested by the existence of the superfluid phase transition.

Recently, Van Leeuwen and Cohen[6] proposed a theoretical phase diagram which simulates the empirical one. They derived it, treating the mixtures of

imperfect Bose-Fermi gases up to the first order with respect to the gas para-meter, while statistics were fully taken into account. In this respect, their work demonstrated the importance of the statistics. As for pressure dependences of the lambda line, the solubility at the absolute zero of temperature, and so forth, however, the theory does not agree with experiment. It is because they neglected the strong inter-particle correlations due to the hard core repulsion.

In this report we limit ourselves to the high-temperature region. Our aim is twofold: to explain the dependence of the lambda temperature on He^3-concentration as well as on pressure, and to gain an insight into mechanisms of the phase separation in connection with the superfluid phase transition.

Let us consider physical origins of the phase separation.

i) Phase separation in He^3-He^4 systems occurs not only in liquid mixtures but also in solid mixtures. In the latter, quantum statistical effects show up through zero point motions, namely, as the difference in molar volumes between the two isotopes. This reflects the difference in mass and statistics, and brings about a phase separation.[7] These quantum statistical effects may be described phenomeno-logically in terms of effective interactions among the isotopes. We call the phase separation due to this mechanism "Interaction Driven Stratification (I.D.S.)". I.D.S. should be present in the liquid mixtures, too.

ii) What is characteristic of the liquid mixtures, however, is the superfluid phase transition. The superfluid phase transition markedly deforms the stratifica-tion curve. The smooth round curve observed in solid He^3-He^4 mixtures, which is rather close to that obtained in the theory of regular solutions, is shifted upwards and meets the lambda line at the critical point, where the curve is not smooth any longer.[3] Theoretically speaking, He^3 impurities constitute an obstacle to the superfluid condensation, because of the excluded volume effect. It partially re-moves the phase coherence of the superfluid. As the temperature is lowered, the loss in the superfluid condensation energy is expected to overcompensates the mixing free energy. This mechanism also gives rise to a phase separation, which may be named "Superfluid Driven Stratification (S.D.S.)".

What are implied by the terms "effective interactions," "I.D.S." and "S.D.S." will be much clarified in the next section, where an explicit formulation of the problem is presented. Our actual analysis will be mainly concerned with S.D.S.

Next, we note that a many-body theoretical investigation of superfluid phase transition is not practicable as yet. But a qualitative explanation has been suc-cessfully given to the pressure dependence of the lambda temperature of pure liquid He^4 by Matsubara and Matsuda[8] (abbreviated to M. M. hereafter). M. M. established the equivalence between a many-boson system with the hard core repulsion and an anisotropic Heisenberg ferromagnet with spin one half, in the framework of a lattice model. The M. M. model offers a quantum mechanical extension of the Ising-model formalism for a classical lattice fluid due to Lee and Yang.[9] We will further generalize the M. M. model to consider the Bose

system containing other classical (non-degenerate) particles. Two equivalent formulations are possible. One is to place two distinct spins, S and s, both of the magnitude one half, at each lattice site.[10] The spin S represents the bosons and is treated in the M. M. scheme, and the other spin s describes the classical particles to which the Lee-Yang scheme is applied. In order to take account of the hard core repulsion between bosons and classical particles, an infinite coupling energy between the two spins should be included at the same site. Namely an interaction Hamiltonian of the form, $I \sum_i (S_i^z + \frac{1}{2}) \times (s_i^z + \frac{1}{2})$ with $I \to +\infty$, is at be added. (Here we follow the convention that the spin up state stands for an occupied state and the spin down for a vacancy. The summation is over the lattice sites.) The other formulation puts a spin of the magnitude unity at each site. The three distinct states, corresponding to the three eigenvalues of the z-component of the spin operator, refer to the occupancy by a boson, the vacancy, and the occupancy by a classical particle, respectively. The latter approach will be made in this report.

In § 3, the generalized lattice model is solved by means of molecular field approximation. Section 4 will be devoted to analyze the molecular-field solution.

We shall obtain a phase diagram which exhibits noticeable features in good accord with experimental observations. The phase separation takes place. One of the two phases after the stratification is a normal fluid and the other a superfluid. The He³-concentration of the former is greater than that of the latter. The lambda temperature, whose expression reduces to that obtained by M. M. when He³ atoms are absent, shows a reasonable dependence on He³-concentration and pressure. The relative positions and orientations of the lambda line, the stratification curves and the critical point also agree with empirical data. These points will be discussed more extensively in §§ 4 and 5.

§ 2. Formulation of the lattice model

The Hamiltonian for a mixture of bosons (called He⁴) and classical particles (called He³) is given by

$$\mathcal{H} = T_4 + T_3 + V, \tag{2·1}$$

where T_4 and T_3 are kinetic energies of He⁴ and He³, respectively. V represents the two-body interaction, including both the hard core and the attractive tail. We are interested in calculating the grand partition function

$$\Xi = \mathrm{Tr} \exp \{ -\beta (\mathcal{H} - \mu_4 N_4 - \mu_3 N_3) \}, \tag{2·2}$$

where μ_α and N_α are the chemical potential and the number of He$^\alpha$ atoms, respectively, and $\beta = 1/k_B T$. Since He³ atoms are treated as classical, T_3 commutes with the rest of the Hamiltonian. Therefore in the expression (2·2), $\mathrm{Tr} \exp (-\beta T_3)$ can be calculated separately, which gives

$$\Xi = \mathrm{Tr} \exp (-\beta \widetilde{\mathcal{H}}), \tag{2·3}$$

where

$$\mathcal{H} = T_4 + V - \mu_4 N_4 - \tilde{\mu}_3 N_3 , \qquad (2\cdot4)$$

$$\tilde{\mu}_3 = \mu_3 + \frac{3}{2}\frac{1}{\beta} \log (m_3/2\pi\beta\hbar^2) , \qquad (2\cdot5)$$

$\hbar$ is the Planck's constant divided by 2π, and m_3 is the mass of He³.

In order to evaluate (2·3), the hard core part in the interaction V should be seriously taken into consideration. At the hard core $\exp(-\beta\mathcal{H})$ vanishes, which reflects the most important effect of the strong inter-particle correlation. One may be able to estimate $\mathcal{E}$ by introducing a lattice space, where operators are defined only at discrete lattice sites and multiple occupancy of a site is completely forbidden. The annihilation and creation operators for He⁴ at the j-th site are denoted by b_j and b_j^+. Similarly we write the number operators for He⁴ and He³ as n_{4j} and n_{3j}. One may pass from the continuum to the discrete lattice space in exactly the same way as M. M. Differentiations in the kinetic energy part are replaced by finite differences and space integrations by summations over discrete lattice sites. Thus

$$\mathcal{H} = \frac{1}{2m_4} \sum_{\langle ij\rangle} \frac{b_i^+ - b_j^+}{d} \cdot \frac{b_i - b_j}{d}$$

$$- v_{44} \sum_{\langle ij\rangle} n_{4i}n_{4j} - v_{33} \sum_{\langle ij\rangle} n_{3i}n_{3j} - 2v_{34} \sum_{\langle ij\rangle} n_{3i}n_{4j}$$

$$- \mu_4 \sum_j n_{4j} - \tilde{\mu}_3 \sum_j n_{3j} , \qquad (2\cdot6)$$

where d is the lattice constant, and $\sum_{\langle ij\rangle}$ denotes a summation over the nearest-neighbor pairs. It is understood that the hard core repulsion, namely, the prohibition of multiple occupancy of a site, is to be taken into account by a kinematical constraint on the operators b, n_3 and n_4, as will be explained below. Consequently the terms of $-v_{\alpha\beta}$ are now supposed to express effective residual (i.e., excluding the hard core repulsion) interactions between He$^\alpha$ and He$^\beta$.

Since there are two species of particles, the complete set of states associated with each lattice site is composed of three states, which may be denoted by three vectors:

$$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \cdots \text{occupied by He}^4$$

$$\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \cdots \text{vacant} , \qquad (2\cdot7)$$

$$\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \cdots \text{occupied by He}^3 .$$

These vectors are eigenstates of the z-component of a spin operator with the magnitude unity, corresponding to the eigenvalues 1, 0 and -1. A He^4 atom is created when the spin–raising operator is operated on the state with $S^z = 0$, but not on the state with $S^z = -1$. Therefore the creation operator for a He^4 atom may be expressed by the spin-raising operator multiplied by a suitable projection operator. The number operators are easily constructed in terms of the operator S^z. Thus the kinematical requirement on the operators due to the hard core repulsion is fulfilled by the following identification:

$$b^+ = \frac{1}{\sqrt{2}} S^z S^+, \qquad b = \frac{1}{\sqrt{2}} S^- S^z,$$

$$n_4 = \tfrac{1}{2} S^z (S^z + 1),$$ (2·8)

$$n_3 = \tfrac{1}{2} S^z (S^z - 1).$$

It is of course easy to check that $b^+ b = n_4$ by the use of the spin algebra.

When (2·8) is substituted into $\widetilde{\mathcal{H}}$, (2·6), one obtains, after some rearrangements,

$$\widetilde{\mathcal{H}} = \mathcal{H}_S + \mathcal{H}_I + \mathcal{H}_G,$$ (2·9)

$$\mathcal{H}_S = -\frac{J}{2\gamma_0} \sum_{\langle ij \rangle} S_i^z S_i^+ S_j^- S_j^z,$$

$$\mathcal{H}_I = -K \sum_{\langle ij \rangle} (S_i^z)^2 (S_j^z)^2 - I \sum_{\langle ij \rangle} S_i^z S_j^z - L \sum_{\langle ij \rangle} (S_i^z)^2 S_j^z,$$ (2·10)

$$\mathcal{H}_G = -H_1 \sum_j S_j^z - H_2 \sum_j (S_j^z)^2,$$

where γ_0 is the number of the nearest-neighbor sites. Some new notations have been introduced:

$$J = \gamma_0 \hbar^2 / m_4 d^2,$$ (2·11)

$$K = \tfrac{1}{4}(v_{44} + v_{33} + 2v_{34}),$$

$$I = \tfrac{1}{4}(v_{44} + v_{33} - 2v_{34}),$$ (2·12)

$$L = \tfrac{1}{2}(v_{44} - v_{33}),$$

$$H_1 = \tfrac{1}{2}(\tilde{\mu}_4 - \tilde{\mu}_3), \qquad H_2 = \tfrac{1}{2}(\tilde{\mu}_4 + \tilde{\mu}_3),$$

$$\tilde{\mu}_4 = \mu_4 - \tfrac{1}{2} J.$$ (2·13)

Now the distinction between S.D.S. and I.D.S. can be stated without ambiguity. In (2·9), $\mathcal{H}_S$ is responsible for the superfluid transition, while $\mathcal{H}_I$ represents the effective interactions and $\mathcal{H}_G$ arises because we work in the grand canonical ensemble. S.D.S. is the phase separation caused by $\mathcal{H}_S + \mathcal{H}_G$, and I.D.S. is that by $\mathcal{H}_I + \mathcal{H}_G$. As mentioned in § 1, we are interested in S.D.S. which is characteristic of the liquid He^3-He^4 mixtures. In the following sections we will neglect $\mathcal{H}_I$ and investigate the properties of S.D.S.

Before closing the section, two remarks are in order.

i)　The Hamiltonian (2·9) is expressed in terms of spin operators. Various physical quantities obtained in the language of magnetism must be translated back into that of liquid mixtures.[8),9)] Let ρ be the reduced density, namely $(N_3+N_4)/N_L$, where N_L is the total number of the lattice sites, and x be the He^3-concentration $N_3/(N_3+N_4)$. From the operator equivalence (2·8), it is immediately seen that

$$\rho = \langle (S^z)^2 \rangle \, ,$$

$$x = \frac{1}{2}\left(1 - \frac{\langle S^z \rangle}{\langle (S^z)^2 \rangle}\right). \tag{2·14}$$

If f is the free energy per spin defined by

$$f = -\frac{1}{\beta N_L}\log \varXi \, , \tag{2·15}$$

then the pressure P of the liquid mixtures is given by

$$P = -\frac{N_L}{\varOmega}f \, , \tag{2·16}$$

where $\varOmega$ is the volume of the mixtures. Also it follows from the identity

$$-\frac{\partial f}{\partial H_2}\bigg)_{\beta,\,H_1} = \langle (S^z)^2 \rangle$$

and Eqs. (2·14) and (2·16) that

$$P = \frac{N_L}{\varOmega}\int_{-\infty}^{H_2} \langle (S^z)^2 \rangle dH_2)_{\beta,\,H_1}\, . \tag{2·17}$$

ii)　The order parameter ξ characterizing the superfluid phase is given by

$$\xi = \langle b \rangle = \frac{1}{\sqrt{2}}\langle S^- S^z \rangle\, . \tag{2·18}$$

In order to assure the existence of nonvanishing ξ, and to make a complete thermodynamic consideration possible, we introduce a fictitious external field H conjugate to ξ.[11)] This adds an off-diagonal interaction Hamiltonian $\mathscr{H}'$ to $\widehat{\mathscr{H}}$:

$$\mathscr{H}' = -H\sum_j b_j{}^+ + \text{h.c.}$$

$$= -\frac{H}{\sqrt{2}}\sum_j S_j{}^z S_j{}^+ + \text{h.c.} \tag{2·19}$$

$\mathscr{H}'$ represents a coupling with an external boson source. The physical situations correspond to the limit $H \to 0$.

§ 3.　Molecular field approximation

We shall apply molecular field approximation to the spin Hamiltonian $\mathscr{H}_S + \mathscr{H}_G + \mathscr{H}'$. That is, the spin operators are first divided into mean values

and deviations from the mean:

$$S^- S^z = \sqrt{2}\xi + (S^- S^z - \sqrt{2}\xi),$$

$$(S^z)^2 = \langle (S^z)^2 \rangle + ((S^z)^2 - \langle (S^z)^2 \rangle), \tag{3.1}$$

$$S^z = \langle S^z \rangle + (S^z - \langle S^z \rangle).$$

Then the terms of the second order in the deviations are discarded. Thus we are left with the molecular field approximant for the free energy per spin:

$$f = -\frac{1}{\beta N_L} \log \mathrm{Tr} \exp\{-\beta(\mathcal{H}_S + \mathcal{H}_G + \mathcal{H}')\}$$

$$\simeq -\frac{1}{\beta} \log \mathrm{Tr} \exp(-\beta h), \tag{3.2}$$

where h is given by

$$h = -\frac{1}{2\sqrt{2}}(a^* S^- S^z + a S^z S^+) - H_2 (S^z)^2 - H_1 S^z + \frac{1}{2}(H_1 + H_2), \tag{3.3}$$

$$a = J\xi + 2H. \tag{3.4}$$

The last constant term in h has been included for computational convenience.

The effective single-site Hamiltonian h may be written in a 3×3 matrix form with respect to the basis vectors (2.7):

$$h = -\frac{1}{2}\begin{bmatrix} H_1 + H_2 & a & 0 \\ a^* & -(H_1 + H_2) & 0 \\ 0 & 0 & H_2 - 3H_1 \end{bmatrix}. \tag{3.5}$$

On diagonalyzing the matrix, one obtains three eigenvalues of h:

$$\frac{1}{2}E, \quad -\frac{1}{2}E, \quad -\frac{H_2 - 3H_1}{2}, \tag{3.6}$$

where

$$E = \sqrt{|a|^2 + (H_1 + H_2)^2}.$$

The unknown quantities ξ, $\langle (S^z)^2 \rangle$ and $\langle S^z \rangle$ are determined by the self-consistency condition:

$$\xi = -\frac{\partial f}{\partial H^*}\bigg)_{H, H_1, H_2, \beta},$$

$$\langle (S^z)^2 \rangle - \frac{1}{2} = -\frac{\partial f}{\partial H_2}\bigg)_{H, H^*, H_1, \beta}, \tag{3.7}$$

$$\langle S^z \rangle - \frac{1}{2} = -\frac{\partial f}{\partial H_1}\bigg)_{H, H^*, H_2, \beta}.$$

When translated back into the language of the liquid mixtures with the aid of Eqs. (2·14) and (2·13), Eqs. (3·7) become

$$\xi = \frac{a}{E} \frac{\sinh \frac{1}{2}\beta E}{\Xi_1} , \qquad (3\cdot8\cdot1)$$

$$1 - \rho = \frac{\cosh \frac{1}{2}\beta E - (\tilde{\mu}_4/E)\sinh \frac{1}{2}\beta E}{\Xi_1} , \qquad (3\cdot8\cdot2)$$

$$1 - \rho x = \frac{2\cosh \frac{1}{2}\beta E}{\Xi_1} , \qquad (3\cdot8\cdot3)$$

where

$$E = \sqrt{|a|^2 + \tilde{\mu}_4^{\,2}},$$

$$\Xi_1 = \exp\{\tfrac{1}{2}\beta(2\tilde{\mu}_3 - \tilde{\mu}_4)\} + 2\cosh \tfrac{1}{2}\beta E ,$$

and $a = J\xi + 2H$ as before.

As is well known, the molecular field approximation is contained within the general scheme of the Landau's theory of the second order phase transition.[12] Following Landau, we will expand the free energy in terms of the order parameter near the superfluid phase transition points. The procedure enables us to obtain explicit forms for the formal expansion coefficients in the Landau's theory and to investigate the properties of the phase transitions analytically. This will be done in the next section.

§ 4. Phase transitions

The free energy f is a function of intensive parameters H, $\tilde{\mu}_4$, $\tilde{\mu}_3$ and β. Because of the possibility of off-diagonal long range order, ξ is not a single-valued function of H, while ξ determines H uniquely. Therefore we prefer to work with ξ as an independent variable instead of H. Eventually we move on to discuss a phase separation. In that occasion relevant variables are the chemical potentials and the temperature, since the stratification curves are determined by the condition that each of the components of the mixtures has a common chemical potential in all the phases in equilibrium at a given temperature. So that we retain $\tilde{\mu}_4$, $\tilde{\mu}_3$ and β as independent parameters.

An appropriate thermodynamic function g may be obtained by a Legendre transformation from f:

$$g = g(\xi, \tilde{\mu}_4, \tilde{\mu}_3, \beta) = f + H\xi . \qquad (4\cdot1)$$

It holds that

$$\left.\frac{\partial g}{\partial \xi}\right)_{\tilde{\mu}_4, \tilde{\mu}_3, \beta} = H . \qquad (4\cdot2)$$

(In this section we choose H and ξ to be real just to avoid extra complications.

The results are independent of the choice of the phases of these parameters.) Equation (3·8·1) shows that H is an odd function of ξ. This equation may be used to construct the following expansion in the vicinity of the superfluid phase transition points:

$$H = 2A\xi + 4B\xi^3 + 6C\xi^5 + \cdots. \qquad (4\cdot3)$$

Using Eqs. (4·2) and (4·3) one obtains

$$g = g_0 + A\xi^2 + B\xi^4 + C\xi^6 + \cdots. \qquad (4\cdot4)$$

The calculation of the coefficients A, B and C is tedious but straightforward. We introduce, for brevity, the following dimensionless variables:

$$t = \frac{4}{\beta J},$$

$$w = \tfrac{1}{2}\beta \tilde{\mu}_4, \qquad (4\cdot5)$$

$$u = \tfrac{1}{2} \exp\{\tfrac{1}{2}\beta (2\tilde{\mu}_3 - \tilde{\mu}_4)\} + \cosh w.$$

Then the coefficients are expessed, in unit of $1/\beta$, as

$$A = \frac{w}{\sinh w} u - \frac{1}{t}, \qquad (4\cdot6\cdot1)$$

$$B = \frac{w}{\sinh^3 w} u^2 \{w \sinh w - u(w \coth w - 1)\}, \qquad (4\cdot6\cdot2)$$

$$C = \frac{2}{3} \frac{w}{\sinh^5 w} u^3 \{u^2 (3 - w^2 - 9w \coth w + 6w^2 \coth^2 w)$$

$$- 9uw \sinh w (w \coth w - 1) + 4w^3 \sinh^2 w\}. \qquad (4\cdot6\cdot3)$$

It is immediately seen that at sufficiently high temperatures A is positive, since $uw/\sinh w > 0$. This should be the case, since at high temperatures there is no spontaneous long range order, and g must have its minimum at $\xi = 0$. In the subsequent analysis we approach the transition points from the normal phase, namely from above in the T-x plane. In the normal phase, density $\rho^{(n)}$ and He³-concentration $x^{(n)}$ are related to the independent variables by

$$2(1 - \rho^{(n)}) = \frac{\cosh w - \sinh w}{u}, \qquad (4\cdot7\cdot1)$$

$$1 - \rho^{(n)} x^{(n)} = \frac{\cosh w}{u}, \qquad (4\cdot7\cdot2)$$

which result from Eqs. (3·8·2) and (3·8·3) when ξ and H vanish. For simplicity we let t, u and w vary, while keeping the normal-phase density $\rho^{(n)}$ constant. Then u can be eliminated and we are left with w and t as independent parameters. The values of B, C and the normal-phase concentration $x^{(n)}$ are
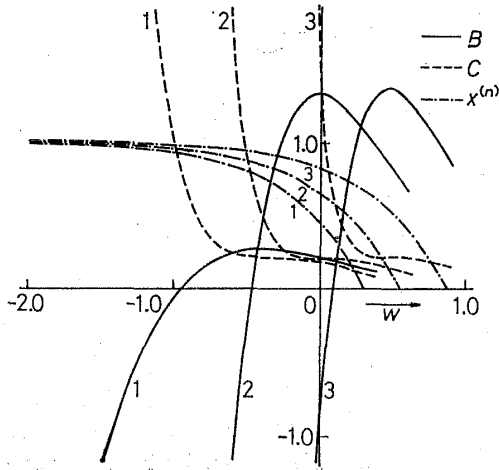
Fig. 1. Plot of B (solid curve), C (dashed curve) and $x^{(n)}$ (dot-dashed curve) versus w for three values of $\rho^{(n)}$. B and C are arbitrarily normalized. The numbers 1, 2 and 3 refer to $\rho^{(n)} = 0.65$, 0.75 and 0.85, respectively. The point where the curve for B crosses the abscissa gives w_c. w is physically meaningful only in the interval where $0 \leq x^{(n)} \leq 1$.

plotted versus w in Fig. 1. It is seen that there are two distinct cases for the behavior of the free energy g depending on the sign of B:

Case (a) For $w > {}^a w_G$ (w_G depends on $\rho^{(n)}$), $B > 0$ and $C > 0$.

As one decreases t, keeping w fixed, A goes through zero at $t = {}^a t_\lambda$ from positive to negative. The behavior of g is described in Fig. 2. It exhibits a continuous transition from a state with $\bar\xi = 0$ to another with $\bar\xi \neq 0$. This may be identified as the superfluid phase transition. Thus the lambda temperature t_λ is determined by

$$A = 0. \qquad (4 \cdot 8)$$

Case (b) For $w < w_G$, $B < 0$ and $C > 0$.

In this case, before t reaches t_λ from above, namely at $t = {}^a t_S > t_\lambda$, A becomes so small and positive that the equation

$$B^2 - 4AC = 0 \qquad (4 \cdot 9)$$

holds. A typical example is shown in Fig. 3 for $\rho^{(n)} = 0.75$ and $w = -0.50$ ($w_G = -0.45$ for this value of $\rho^{(n)}$). When Eq. (4·9) holds, g is equal to g_0 both at $\bar\xi = 0$ and $\bar\xi = \bar\xi_S \equiv (-2A/B)^{1/2}$. Thus the free energy g behaves in quite a different manner from case (a) (see Fig. 4). We see that a discontinuous transition occurs at $t = t_S$ from a phase with $\bar\xi = 0$ to another with $\bar\xi = \bar\xi_S$. These two phases coexist at $t = t_S$ with the same values of the chemical poten-
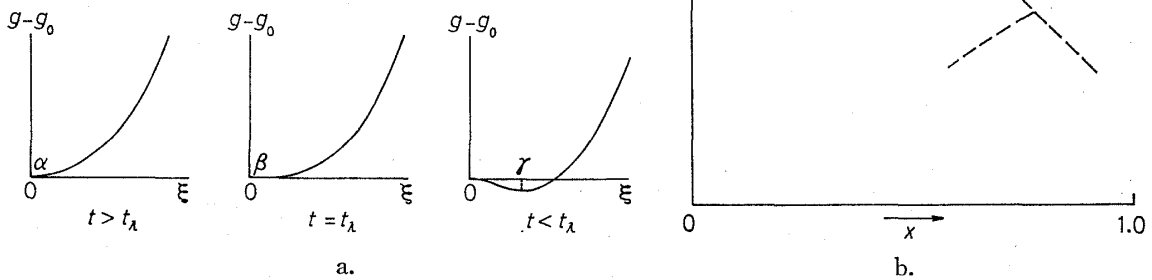

Fig. 2. a. Behavior of g for $w > w_c$ as the temperature is lowered. b. Locus of the equilibrium point corresponding to the minimum point of g.

tials, since the curves for g are drawn at con-
stant u, w and t. The transition, therefore,
corresponds to the phase separation into a
normal and a superfluid phases. It is also clear
from the foregoing arguments that the strati-
fication temperature t_s is determined by Eq.
(4·9), and that $t_s > t_\lambda$, where t_λ implies the
virtual lambda temperature when $w < w_c$. (The
superfluid phase transition does not occur for
$w < w_c$. Consequently t_λ does not actually exist.
But one may formally extend the curve
determined by Eq. (4·8) into this region. The
extended part of the curve is called the virtual
lambda line. See Fig. 5.)

Fig. 3. Relation among A, B and C
for $\rho^{(n)} = 0.75$ and $w = -0.50$ as t
is varied. Qualitative features are
the same for other values of $\rho^{(n)}$
and $w (< w_c)$.

A critical point appears between the above two cases, and is determined by

$$A = B = 0 . \tag{4·10}$$

This critical point marks the termination of the superfluid phase transition line
and the subsequent onset of the phase separation. Thus it may be identified
with the critical point observed experimantally.

The rest of the section will be devoted to a detailed analysis of the phase
transitions based on the equations derived above.

i) *Lambda line*

Along the lambda line the order para-
meter ξ vanishes. Hence Eqs. (4·7) may
be used to replace u and w in Eq. (4·8)
with ρ and x measured along the lambda
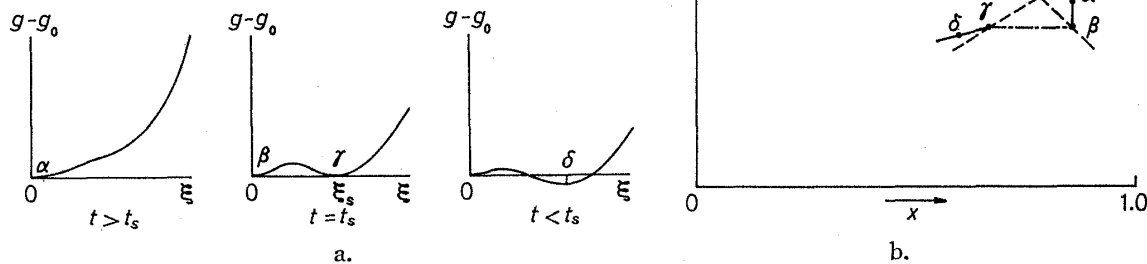line. From Eqs. (4·7),

Fig. 4. a. Behavior of g for $w < w_c$ as the temperature is lowered. b. Locus of the equi-
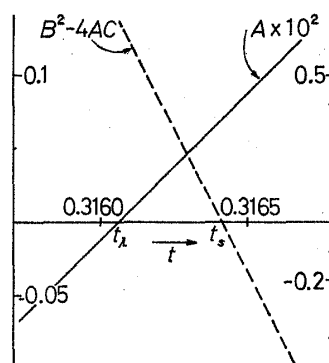librium point corresponding to the minimum point of g.

$$\frac{\sinh w}{u} = 2\rho(1-x) - (1-\rho x),$$

$$\tanh w = \frac{2\rho(1-x) - (1-\rho x)}{1-\rho x},$$

while Eqs. (4·6·1) and (4·8) give

$$w = \frac{1}{t_\lambda} \frac{\sinh w}{u}.$$

Combining these three equations, one obtains

$$2\rho(1-x) - (1-\rho x) = (1-\rho x)\tanh\frac{1}{t_\lambda}\{2\rho(1-x) - (1-\rho x)\}. \qquad (4·11)$$

This formula reduces to that by M. M. when $x=0$. It is to be remarked that, if a simple substitution $\rho \to \rho_4 = \rho(1-x)$ is made in the M. M. formula, then t_λ increases with x for small x (we assume $\rho > 1/2$ as in M. M. since we are concerned with a liquid state). In (4·11), the correlation factor $(1-\rho x)$ guarantees that t_λ is a decreasing function of x. It takes account of the excluded volume effect exactly, apart from a possible resonance effect which cannot be treated within the molecular field approximation. As for the pressure or density dependence, the lambda line shifts downwards with increasing ρ (see Fig. 5).
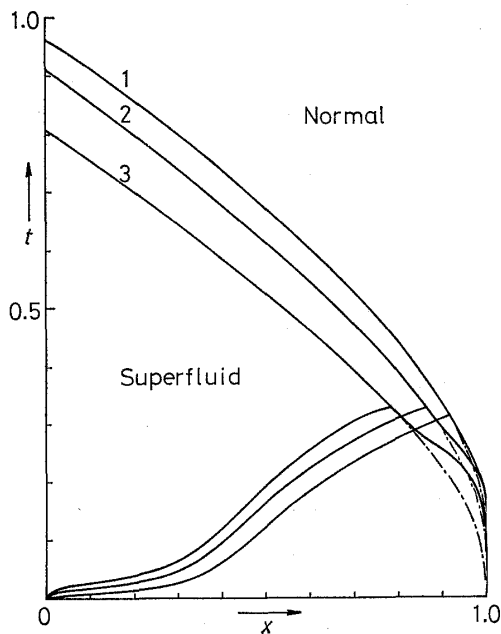

Fig. 5. Theoretical phase diagrams for various values of ρ. At each curve ρ is kept constant all along the lambda line and the normal-phase boundary. The numbers 1, 2 and 3 refer to $\rho=0.65$, 0.75 and 0.85, respectively. The dot-dashed curves give the virtual lambda lines.
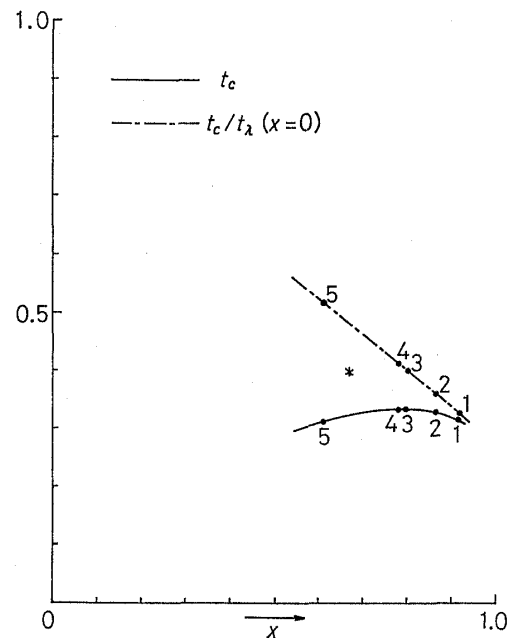
Fig. 6. Migration of the critical point (solid curve) and the reduced critical point (dot-dashed curve) as ρ is varied. The points numbered 1, 2, 3, 4 and 5 refer to $\rho=0.65$, 0.75, 5/6, 0.85 and 0.95. The empirical reduced critical point taken from Ref. 3) is marked by an asterisk.

ii) *Critical point*

Equations (4·6) and (4·10) give

$$w = \frac{1}{t_\sigma} \frac{\sinh w}{u},$$

$$u = \frac{w \sinh w}{w \coth w - 1}$$

with $w = w_\sigma$. Since $\xi = 0$ at the critical point, u and w_σ are again related to ρ and x at the critical point by Eqs. (4·7). Elimination of u yields the following dependence of t_σ and x_σ on ρ in a parametrized form:

$$t_\sigma = \frac{w \coth w - 1}{w^2},$$

$$x_\sigma = 2 \frac{w - (w \coth w - 1) \coth w}{2w - (w \coth w - 1)(\coth w - 1)}, \qquad (4·12)$$

$$2(1 - \rho) = \frac{(w \coth w - 1)(\coth w - 1)}{w}.$$

The quantities x_σ and ρ are decreasing and increasing functions of w, respectively, while t_σ is an even function of w. Thus, as ρ increases, t_σ increases for $\rho < 5/6$ ($\rho = 5/6$ corresponds to $w = 0$, $t_\sigma = 1/3$ and $x_\sigma = 0.8$), and decreases for $\rho > 5/6$, whereas x_σ is a decreasing function of ρ. Figure 6 shows the migration of the critical point in $T\text{-}x$ plane as ρ is varied. Also shown there is the migration of the reduced critical point $(t_\sigma/t_\lambda(x=0), x_\sigma)$. We also note that $x_\sigma \leq 1/2$ only when $\rho > 0.98$. Therefore the critical point is practically always in the right half of $T\text{-}x$ plane. This is one of the remarkable properties of S.D.S.

iii) *Phase separation*

Just below the critical point, Eq. (4·9) determines the stratification curves. If we fix $\rho^{(n)}$ and $t = {}^{\alpha}t_S(<t_\sigma)$, then Eqs. (4·7·1) and (4·9) uniquely specify the values of u and w. Then $x^{(n)}$ is obtained from Eq. (4·7·2), which gives the stratification curve corresponding to the normal-phase boundary. Next, the same values of u and w, or $\tilde{\mu}_4$ and $\tilde{\mu}_3$, together with ξ_S calculated from these, should be put into Eqs. (3·8·2) and (3·8·3) with $H = 0$, to obtain the density $\rho^{(s)}$ and the He³-concentration $x^{(s)}$ of the coexisting superfluid phase. In this way we get the other stratification curve corresponding to the superfluid-phase boundary. We have carried out the procedure numerically. The results are shown in Fig. 5. The superfluid-phase boundary finds itself to the left of the virtual lambda line. The normal-phase boundary joins smoothly to the lambda line, which is a general feature of the molecular field approximation.[12] At lower temperatures far from the critical point, expansion in power series of ξ is im-

possible and we have to numerically analyze Eqs. (3·8) directly. Our model loses its validity in this region.

§ 5. Concluding remarks

The following results have been obtained in a unified manner within the framework of a generalized lattice model and molecular field approximation:

1) There occur two kinds of phase transition: The superfluid phase transition and phase separation.

2) The lambda line terminates just at the critical point of the phase separation.

3) The lambda temperature is a decreasing function both of He^3-concentration and density.

4) When the phase separation takes place, two phases coexist: one is normal and the other superfluid. At constant temperature, the normal-phase boundary is located to the right of the virtual lambda line, and the superfluid-phase boundary to the left. At constant He^3-concentration, the normal-phase boundary lies above the virtual lambda line.

5) The critical point lies in the right half of the phase diagram.

These properties are all in qualitative agreement with empirical data. Thus it is seen that S.D.S. alone is sufficient to explain important general features of the phase diagram. However, when one asks about subtler problems, such as the density dependence of the position of the critical point or the magnitude of x_C, I.D.S. cannot be neglected. In solid He^3-He^4 mixtures,[7] where I.D.S. alone is operative, x_C is slightly less than one half. As the pressure is increased, T_C decreases slightly while x_C is expected to increase toward one half, because pressure reduces the difference in molar volumes between the isotopes. This effect should be more enhanced in the liquid mixtures, where the molar-volume difference is larger. Then it may well be that rather large values of x_C (see Fig. 5) get reduced by I.D.S. Also the density dependence of the position of the critical point (see Fig. 6) might be compensated by I.D.S., resulting in a monotonous decrease in t_C with little change in x_C. More clear-cut experimental data than presently available[13] are desired on the behavior of the critical point.

Some generalizations of our theory may be conceived:

a) To include $\mathcal{H}_I$ and discuss I.D.S. together with S.D.S. (It is easy to check that, within molecular field approximation, the inclusion of $\mathcal{H}_I$ does not alter the formula for the lambda line, Eq. (4·11).)

b) To go beyond molecular field approximation.

c) To take the Fermi statistics into account and treat the low-temperature region.[14]

Recently Blume, Emery and Griffiths[15] proposed a spin-one Ising model for He^3-He^4 mixtures. They carried out a similar analysis on their model as we

have done here. As the authors admit it, however, the significance of their order parameter is not clear. It seems to be more natural to interpret that they treated a gas-liquid transition of one of the components of a binary mixture, while the other component has much lower gas-liquid critical temperature.

Acknowledgements

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