

## Ising Model for the $\lambda$ Transition and Phase Separation in $\text{He}^3\text{-He}^4$ Mixtures\*

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A spin-1 Ising model, which simulates the thermodynamic behavior of  $\text{He}^3\text{-He}^4$  mixtures along the  $\lambda$  line and near the critical mixing point, is introduced and solved in the mean-field approximation. For reasonable values of the parameters of the model the phase diagram is qualitatively similar to that observed experimentally and the phase separation appears as a consequence of the superfluid ordering. Changing the parameters produces many different types of phase diagram, including as features  $\lambda$  lines, critical points, tricritical points, and triple points. Certain thermodynamic features which differ from the  $\text{He}^3\text{-He}^4$  experiments may be artifacts of the mean-field theory.

### I. INTRODUCTION

The general features of phase separation and superfluidity in mixtures of liquid  $\text{He}^3$  and  $\text{He}^4$  have been known for some time.<sup>1,2</sup> For  $\text{He}^3$  concentration below 67%, the mixture is able to support a  $\lambda$  transition, but, at higher concentrations, it undergoes a first-order transition into two phases, of which only the  $\text{He}^4$ -rich phase is superfluid. In this paper we present a simplified model involving an Ising spin system with a spin  $S = 1$  at each lattice site, which reproduces at least qualitatively the main features of the phase diagram for the superfluid and phase-separation transitions. Details of the model are given in Sec. II and results from solving it in the mean-field approximation are found in Sec. III.

Although the model has some unphysical features, we feel nonetheless that it gives some insight into the peculiar thermodynamic behavior of helium mixtures and tends to confirm the conclusion reached earlier by van Leeuwen and Cohen<sup>3</sup> that the phase separation is intimately related to the tendency toward superfluid ordering in  $\text{He}^4$ . Furthermore, our model, which is a type of classical "lattice gas," is amenable to investigation by the techniques of exact series expansions which have proved very fruitful in studies of phase transitions.<sup>4</sup> Thus there is at least the possibility (which we ourselves have not investigated) that the mean-field results presented below can be considerably refined and improved.

### II. ISING LATTICE MODEL

Our model for  $\text{He}^3\text{-He}^4$  mixtures consists of a discrete lattice and a fictitious spin variable  $S_i$ , taking the values 0 and  $\pm 1$ , associated with each lattice site. A  $\text{He}^3$  atom at site  $i$  corresponds to  $S_i = 0$  and a  $\text{He}^4$  atom to  $S_i = \pm 1$ . There is one and

only one atom at each site and the model makes no allowances for vacancies. The additional degree of freedom, the sign of  $S_i$ , associated with a  $\text{He}^4$  atom, is introduced simply for the purpose of providing an "order parameter," viz., the thermal average of the total spin

$$M = N^{-1} \sum_{i=1}^N \langle S_i \rangle, \quad (2.1)$$

which in our model corresponds to the superfluid order parameter of liquid helium.<sup>5</sup> Of course  $M$  has only two possible phases, positive and negative, whereas the phase of the order parameter for liquid helium can be varied continuously. This is only one of the unphysical features of our model. Our purpose, however, is not to give a correct description of the microscopic behavior of helium mixtures but merely to show that the possibility of an additional order parameter for one of the species ( $\text{He}^4$ ) and not for the other is by itself enough to account for several features of the observed phase diagram.

The number of  $\text{He}^3$  and  $\text{He}^4$  atoms are given by

$$\hat{N}_3 = \sum_i^N (1 - S_i^2), \quad (2.2)$$

$$\hat{N}_4 = \sum_i^N S_i^2, \quad (2.3)$$

with  $\hat{N}_3 + \hat{N}_4 = N$ , the total number of sites. The  $\text{He}^3$  concentration

$$x = \langle \hat{N}_3 \rangle / N \quad (2.4)$$

is an additional order parameter which reflects the possibility of phase separation.

For a translationally invariant system, we have

$$M = \langle S_i \rangle \quad (2.5)$$

and

$$x = 1 - \langle S_i^2 \rangle. \quad (2.6)$$

Here  $\langle S_i \rangle$  and  $\langle S_i^2 \rangle$  are, respectively, the magnetization and mean quadrupole moment of the fictitious spin system, and superfluid ordering and phase separation in the mixture are simulated by magnetic ordering and quadrupolar ordering in the model.

The model Hamiltonian consists of two terms: The first is

$$H_S = -J \sum_{\langle i,j \rangle} S_i S_j, \quad (2.7)$$

where the summation is over nearest-neighbor pairs. This term is responsible for the "superfluid" ordering since it leads to a second-order transition in which a nonzero value of  $M$  appears at a critical temperature  $T_c$  determined by the "exchange" integral  $J$  and the concentration of  $\text{He}^3$  atoms. When the concentration of  $\text{He}^3$  is zero, all  $S_i = \pm 1$ , and  $H_S$  in Eq. (2.7) becomes the usual Hamiltonian for an Ising ferromagnet. The presence of the  $\text{He}^3$  means that a number of the  $S_i^2$  are zero, which is similar to the inclusion of nonmagnetic impurities in the fictitious spin system, and discourages the transition, so that  $T_c$  decreases. This is qualitatively in accord with experiment. In addition it will be shown that when  $x$  is sufficiently large, the system can only continue to support the superfluid ordering by breaking into two phases, with the  $\text{He}^3$ -rich phase remaining in the normal state. According to Eq. (2.6) this is equivalent to quadrupolar ordering in the model.

In this case, phase separation is a direct consequence of the superfluid ordering, but, as in a mixture of classical fluids, it could also be induced directly by the interaction between components without the benefit of superfluidity, and it is of interest to compare the two mechanisms theoretically. For this reason an interaction term

$$H_I = -K_{33} \sum_{\langle i,j \rangle} (1 - S_i^2)(1 - S_j^2) - K_{44} \sum_{\langle i,j \rangle} S_i^2 S_j^2 - K_{34} \sum_{\langle i,j \rangle} [S_i^2(1 - S_j^2) + S_j^2(1 - S_i^2)], \quad (2.8)$$

will be included in the Hamiltonian. Here again the summation is over nearest-neighbor pairs, and since  $S_i^2$  is zero for  $\text{He}^3$  and unity for  $\text{He}^4$ ,  $-K_{\alpha\beta}$  is the effective  $\text{He}^\alpha$ - $\text{He}^\beta$  interaction. The terms in Eq. (2.8) may be rearranged to give

$$H_I = -(K_{33} + K_{44} - 2K_{34}) \sum_{\langle i,j \rangle} S_i^2 S_j^2 - 2z(K_{34} - K_{33}) \sum_i S_i^2 - zNK_{33}, \quad (2.9)$$

where  $z$  is the number of nearest neighbors for the lattice. Of course, there is the same interatomic force between all He atoms but, in the liquid, differences of mass and statistics lead to different effective interactions between  $\text{He}^3$  atoms and  $\text{He}^4$  atoms<sup>6</sup> and this is reflected in the differences be-

tween the  $K_{\alpha\beta}$ . If the  $K_{\alpha\beta}$  were equal,  $H_I$  would reduce to a constant; if they were nearly equal, the variable part of  $H_I$  would be a small perturbation.

Since  $\langle \hat{N}_3 \rangle$  and  $\langle \hat{N}_4 \rangle$  are given, it is then necessary to introduce chemical potentials  $\mu_3$  and  $\mu_4$  for the  $\text{He}^3$  and  $\text{He}^4$ , respectively, and they may be incorporated into the total Hamiltonian

$$\mathcal{H} = H_S + H_I - \mu_3 \hat{N}_3 - \mu_4 \hat{N}_4, \quad (2.10)$$

which may be rewritten

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} S_i S_j - K \sum_{\langle i,j \rangle} S_i^2 S_j^2 + \Delta \sum_i S_i^2 - N(zK_{33} + \mu_3) \quad (2.11)$$

from Eqs. (2.2), (2.3), (2.7), and (2.9). Here, we have

$$K = K_{33} + K_{44} - 2K_{34} \quad (2.12)$$

and

$$\Delta = \mu_3 - \mu_4 + 2z(K_{33} - K_{44}). \quad (2.13)$$

The model Hamiltonian  $\mathcal{H}$  represents a spin-1 Ising model with biquadratic exchange of strength  $K$  and a crystal field of strength  $\Delta$ . The constant term on the right-hand side of Eq. (2.11) will be disregarded.

If in Eq. (2.11) we take  $K=0$ , the Hamiltonian becomes that for the spin-1 Ising model with crystal field interaction. The spin term proportional to  $\Delta$  gives single-spin energy levels with an  $S_i = 0$  singlet level lowest and  $S_i = \pm 1$  degenerate and at an energy  $\Delta$  above the singlet (for  $\Delta > 0$ ). Systems of this type have been studied (with application to magnetism in mind) by Blume<sup>7</sup> and Capel<sup>8</sup> in the molecular field approximation, and by Blume and Watson<sup>9</sup> for the equivalent case of infinite-range interactions. These authors have shown that the order-disorder transition becomes, for a critical value of  $\Delta$ , a first-order transition. With our "lattice-gas" interpretation of (2.11) we will show that this onset of a first-order transition is equivalent to phase separation, and we may calculate some properties of the consolute point in the molecular field approximation. The system with  $K=0$  describes phase separation driven by superfluid ordering. The opposite extreme, with  $J=0$ , describes separation driven by the energetics of particle-particle interactions. This Hamiltonian has been treated by Griffiths,<sup>10</sup> who showed that the statistical mechanics of this system could be reduced to that of the spin- $\frac{1}{2}$  Ising model in a temperature-dependent external magnetic field. He showed that for certain values of  $\Delta$ , a first-order phase transition (in this case, in the order parameter  $x$ ) occurs. These exact results are very close to those obtained in the molecular field approximation, and they also predict a region of phase separation. We shall be concerned primarily with the case of  $|K| \ll |J|$ , as this corresponds most closely to the experimental

situation, but we will consider briefly the case of  $K$  large as well.

Further consideration of (2.11) shows that the term  $\Delta \sum_i S_i^2$  corresponds to an external "field" coupling to the order parameter  $x$ . We might also add to (2.11) a term  $H \sum_i S_i$  coupling to the order parameter  $M$ . In a magnetic system this of course represents an external magnetic field coupled to the magnetization, but in a superfluid there is no direct physical analog of such a field. We may nevertheless consider the mathematical effect of such a term on the phase diagram of the system, and we do so in Sec. III.

### III. MOLECULAR FIELD APPROXIMATION

The most direct way of deriving the molecular field approximation is to use the variation principle for the free energy<sup>11</sup>

$$F \leq \Phi \equiv \text{Tr} \rho \mathcal{H} + (1/\beta) \text{Tr} \rho \ln \rho, \quad (3.1)$$

where  $F$  is the exact free energy and  $\rho$  is any trial density matrix. The equality sign holds if  $\rho = \exp(-\beta \mathcal{H}) / [\text{Tr} \exp(-\beta \mathcal{H})]$ , the equilibrium density matrix for the system.

To obtain the molecular field approximation, it is assumed that

$$\rho = \rho_0 \equiv \prod_i \rho_i, \quad (3.2)$$

where  $\rho_i$  is the single-spin density matrix for site  $i$ . For a translationally invariant system,  $\rho_i$  is independent of  $i$  and is equal to say  $\rho_1$ . Then substituting Eqs. (2.11) and (3.2) into Eq. (3.1),

$$\begin{aligned} \Phi/N = & -\frac{1}{2} \mathcal{J} (\text{Tr} \rho_1 S_1)^2 - \frac{1}{2} \mathcal{K} (\text{Tr} \rho_1 S_1^2)^2 \\ & + \Delta \text{Tr} \rho_1 S_1^2 + (1/\beta) \text{Tr} \rho_1 \ln \rho_1, \end{aligned} \quad (3.3)$$

where  $\mathcal{J} = zJ$  and  $\mathcal{K} = zK$ .

To obtain the best form of  $\rho_1$  with  $\text{Tr} \rho_1 = 1$ , it is necessary to minimize  $\Phi/N + \lambda \text{Tr} \rho_1$  with respect to  $\rho_1$ . Differentiating Eq. (3.3) with respect to  $\rho_1$  and evaluating  $\lambda$ , it is found that

$$\rho_1 = e^{-\beta h} / \text{Tr} e^{-\beta h}, \quad (3.4)$$

where the single-spin molecular field Hamiltonian  $h$  is given by

$$h = -\mathcal{J} (\text{Tr} \rho_1 S_1) S_1 - \mathcal{K} (\text{Tr} \rho_1 S_1^2) S_1^2 + \Delta S_1^2 \quad (3.5)$$

$$= -\mathcal{J} M S_1 + [\Delta - \mathcal{K}(1-x)] S_1^2, \quad (3.6)$$

using the definitions (2.5) and (2.6). Now  $M$  and  $x$  have to be evaluated from Eqs. (2.5), (2.6), (3.4), and (3.6) to give

$$1-x = \frac{2 \cosh \beta \mathcal{J} M}{\exp\{\beta[\Delta - \mathcal{K}(1-x)]\} + 2 \cosh \beta \mathcal{J} M}, \quad (3.7)$$

$$M = \frac{2 \sinh \beta \mathcal{J} M}{\exp\{\beta[\Delta - \mathcal{K}(1-x)]\} + 2 \cosh \beta \mathcal{J} M}. \quad (3.8)$$

In a mixture,  $x$  is specified and  $M$  and  $\Delta$  (which contains  $\mu_3$  and  $\mu_4$ ) are to be determined from these self-consistent equations. However, in considering phase separation, we are looking for two phases with different values of  $x$  but the same  $\mu_3$  and  $\mu_4$ , and hence the same  $\Delta$ . For this reason, it is analytically simpler to assume that  $\Delta$  is given and to solve Eqs. (3.7) and (3.8) for  $M$  and  $x$ . The same procedure would be followed automatically in a magnetic system where  $\Delta$  is a prescribed field.

There will, in general, be several pairs of solution  $(M, x)$  for (3.7) and (3.8), and the pair chosen is that which minimizes  $\Phi$  in (3.3). There will always be one set of solutions with  $M=0$  and with  $x$  given by the solution of

$$1-x = \frac{2}{\exp\{\beta[\Delta - \mathcal{K}(1-x)]\} + 2}, \quad M=0. \quad (3.9)$$

In addition, there may be solutions with  $M \neq 0$ . To find these we note that, for  $M \neq 0$ , it is possible to divide (3.7) by (3.8) to obtain

$$1-x = M \coth \beta \mathcal{J} M, \quad M \neq 0. \quad (3.10)$$

Substitution of (3.10) in (3.8) then yields an equation for  $M$ .

The regions in which  $M=0$  or  $M \neq 0$  are separated in the  $T$ - $x$  plane by a line of phase transitions, as shown in Fig. 1. In most parts of this diagram it is necessary to solve for  $x$  and  $M$  numerically, as described above, but the neighborhood of this line can be discussed analytically.

*a.  $\mathcal{K}=0$ .* We first consider the case  $\mathcal{K}=0$ , which is less complicated and quite close to the experimental situation.

For this argument we suppose that a small "magnetic field"  $H$  is applied to the system to ensure that  $M \neq 0$  everywhere. This means that  $\mathcal{J}M$  is replaced by  $(\mathcal{J}M - H)$  in Eq. (3.6) and hence also in Eqs. (3.7)–(3.10). The thermodynamic potential  $G(M)$  is given by

$$G(M) = \Phi - MH \quad (3.11)$$

and

$$H = -\frac{\partial G}{\partial M}, \quad (3.12)$$

so that, for  $H=0$ ,  $G$  is a minimum with respect to  $M$ . In the molecular field approximation,  $G$  is analytic in  $M$  and may be expanded in the form

$$G = G_0 + AM^2 + BM^4 + CM^6 + \dots, \quad (3.13)$$

where  $G_0$  and the coefficients  $A$  and  $B$  are functions of  $\beta$  and  $\Delta$ .

For  $\mathcal{K}=0$  and  $H \neq 0$ , Eq. (3.8) becomes

$$M = 2 \sinh \beta (\mathcal{J}M - H) / [e^{\beta \Delta} + 2 \cosh \beta (\mathcal{J}M - H)] \quad (3.14)$$

and it is quite straightforward to use this equation to find  $H$  as a series in powers of  $M$  and so to find

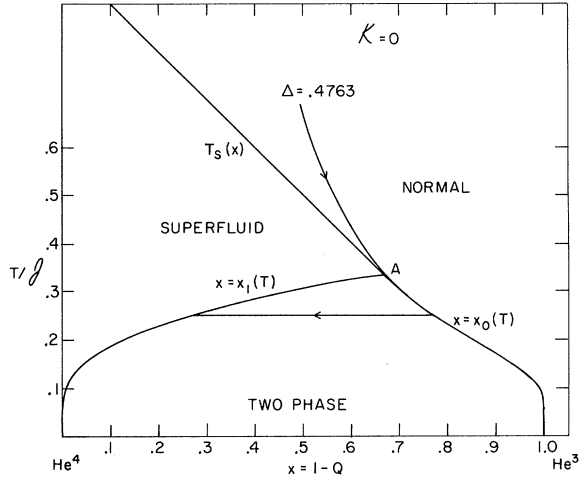


FIG. 1. Phase diagram for He<sup>3</sup>-He<sup>4</sup> mixtures as predicted by the mean-field calculation with  $\mathcal{K}=0$ . The tricritical point  $A$  separates the second-order transition region from the first-order region. A line of constant  $\Delta$  is shown. For  $T$  slightly above and below the transition temperature, this line is extremely close to the phase-separation curves and is indistinguishable from them on the figure.

$A$  and  $B$  by comparison with Eqs. (3.12) and (3.13). In this way

$$A = \delta/2\beta - \frac{1}{2}\mathcal{J}, \quad (3.15)$$

$$B = (1/8\beta)(\delta^2 - \frac{1}{3}\delta^3), \quad (3.16)$$

$$C = (1/6\beta)(\frac{1}{2}\delta^3 - \frac{3}{8}\delta^4 + \frac{3}{40}\delta^5), \quad (3.17)$$

where

$$\delta = 1 + \frac{1}{2}e^{\beta\Delta}. \quad (3.18)$$

Equation (3.13) is the form assumed in Landau's theory of phase transitions.<sup>12</sup> From Eq. (3.12), when  $H=0$ ,  $G$  has to be a minimum with respect to variations of  $M$ . When  $A > 0$ ,  $B > 0$ , the minimum occurs at  $M=0$ . When  $A < 0$ ,  $M=0$  is a maximum and the equilibrium  $M$  has a finite value. Thus the "superfluid" ordering temperature,  $T_S(x)$  in Fig. 1, is determined by  $A=0$  or, from Eqs. (3.15) and (3.9),

$$\frac{1}{\beta_S\mathcal{J}} = \frac{T_S(x)}{\mathcal{J}} = \frac{1}{1 + \frac{1}{2}e^{\beta\Delta}} \quad (3.19)$$

$$= 1 - x. \quad (3.20)$$

In particular, at  $x=0$ ,  $T_S(0)=\mathcal{J}$  in our approximation. As the He<sup>3</sup> concentration  $x$  is increased,  $T_S$  decreases linearly from its value  $\mathcal{J}$  for pure He<sup>4</sup>. If  $\Delta$  were prescribed instead of  $x$ , pure He<sup>4</sup> would correspond to  $\Delta = -\infty$ , and  $T_S$  would decrease as  $\Delta$  increased. Eventually, when  $x$  and  $T$  have critical values  $x_c$  and  $T_c$ ,  $B$  becomes equal to zero as well as  $A=0$ , and the transition changes to one of first order.<sup>7</sup> From Eqs. (3.16) and (3.19), this occurs

at a temperature  $T_c$  and concentration  $x_c$  such that

$$T_c/T_S(0) = 1 - x_c = \frac{1}{3}. \quad (3.21)$$

Experimentally,<sup>2</sup>  $T_c/T_S(0)$  is 0.4 but  $1 - x_c$  is  $0.331 \pm 0.005$ .

For  $\Delta > \Delta_c$ , as  $T$  is decreased,  $G$  reaches the form shown in Fig. 2 before  $A$  becomes equal to zero. Minima occur at two points,  $M=0$  and  $M_0$  with the same free energy, and the mixture separates into two phases. The He<sup>3</sup>-rich phase has  $M=0$ . Near  $T_c$ , Eq. (3.13) may be used and  $G$  has to be

$$G = G_0 + CM^2(M^2 - M_0^2)^2 \quad (3.22)$$

on the phase-separation curve, so that it has the form shown in Fig. 2. This requires

$$B^2 = 4AC, \quad (3.23)$$

which replaces  $A=0$  as the condition which gives for the superfluid ordering temperature  $T_S$  as a function of  $\Delta$ . Since  $C > 0$ , it follows that  $A > 0$  at  $T_S$  and for  $\Delta > \Delta_c$  the phase-separation curve lies above the line given in Eq. (3.20). Differentiating Eq. (3.23) with respect to  $\Delta$  and letting  $T \rightarrow T_c$ ,

$$\left( \frac{\partial A}{\partial \Delta} + \frac{\partial A}{\partial T_S} \frac{\partial T_S}{\partial \Delta} \right)_{T_S=T_c} = 0 \quad (3.24)$$

determines the slope of  $T_S(\Delta)$  for  $T_c = T_c -$ . But it is also given by the same equation (obtained by differentiating  $A=0$ ) when  $T = T_c +$ . Hence  $\partial T_S/\partial \Delta$  is continuous at  $T_c$ . Then from Eqs. (3.19) and (3.20), which refer to the He<sup>3</sup>-rich end of the phase-separation curve since they assume  $M=0$ ,  $\partial T_S/\partial x$  is continuous at  $T_c$ . This is a feature of classical theories of second-order phase transitions<sup>12</sup> and apparently does not agree with experiment.<sup>2</sup> It is undoubtedly a consequence of the molecular field approximation made here, and the actual behavior of the nearest-neighbor spin-1 Ising model may well differ from that obtained in the molecular field approximation.

The phase boundaries  $T = T_1(x)$  and  $T = T_0(x)$

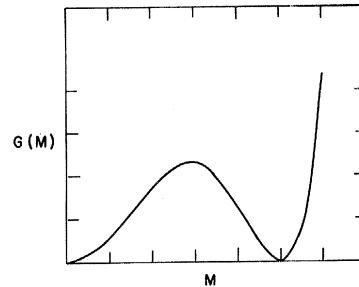


FIG. 2. Free energy as a function of the order parameter  $M$  for the temperature at which a first-order transition occurs. The phase with  $M=0$  is in equilibrium with the phase at the minimum of  $G(M)$  with  $M \neq 0$ .

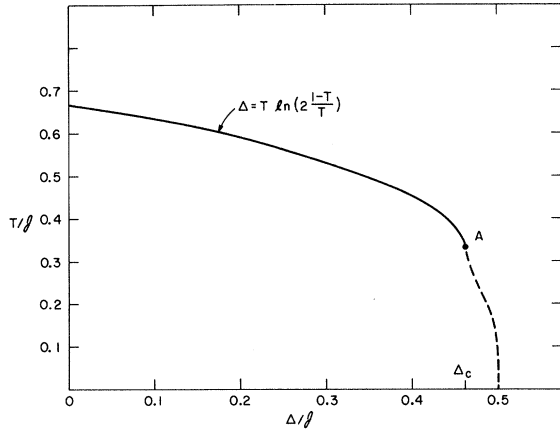


FIG. 3. Phase diagram in the  $T$ - $\Delta$  plane for the mean-field solution with  $\mathcal{K}=0$ . The solid lines represent second-order transitions; dashed lines represent those of first-order. The tricritical point is, as in Fig. 1, denoted by A.

shown in Fig. 1 are derived for  $T \approx T_c$  from Eqs. (3.23), (3.9), and (3.10) with  $M = M_0$ . At lower temperatures the curves have been determined by numerical evaluation. The qualitative features of the experimental phase diagram are reproduced by the molecular field approximation with the exception of the finite (6%) miscibility of  $\text{He}^3$  in  $\text{He}^4$  at  $T = 0^\circ\text{K}$ . It is necessary to include the Fermi statistics for  $\text{He}^3$  in order to reproduce this feature.<sup>6</sup>

It is also of interest to consider the phase diagram in the  $T$ - $\Delta$  plane, as shown in Fig. 3. Here the second-order transition (superfluid ordering) starts at  $\Delta = -\infty$  and  $T = \beta$  (pure  $\text{He}^4$ ) and decreases in temperature as  $\Delta$  increases. At  $\Delta_c = \beta \frac{2}{3} \ln 2 = 0.4621\beta$ ,  $T_c = \frac{1}{3}\beta$ , the transition changes to first order, and since  $\Delta$  is the same in the two coexisting phases, the first-order phase boundary is a single line in the  $T$ - $\Delta$  plane rather than the two lines in the  $T$ - $x$  plane. As one of us pointed out previously,<sup>13</sup> if one looks in  $(T, \Delta, H)$  space, the first-order phase-transition line in the  $T$ - $\Delta$  plane is a line of triple points where two first-order transitions occurring from finite  $H$  meet the first-order transition surface (where  $M$  is discontinuous) in the  $T$ - $\Delta$  plane, the region lying below the curve  $T_s(\Delta)$ . From this point of view, the curve  $T_s(\Delta)$  is a line of "critical points" (terminating a first-order phase-transition surface) which at  $T = T_c$  and  $\Delta = \Delta_c$  is joined by two other lines of critical points terminating the first-order phase-transition surfaces for  $H > 0$  and  $H < 0$ . (This confluence of three lines of critical points led to the suggestion<sup>13</sup> that  $T = T_c$ ,  $\Delta = \Delta_c$ , and  $H = 0$  be called a "tricritical" point.)

The equations for the lines of critical points are

easily determined. They are given by ( $\beta = 1$ )

$$\left. \begin{aligned} \Delta &= T \ln [2(1-T)/T] \\ H &= 0 \end{aligned} \right\}, \quad \frac{1}{3} \leq T \leq 1$$

which is found by setting  $H = 0$  and, in Eq. (3.15),  $A = 0$ . For  $H \neq 0$ , conditions  $\partial H / \partial M = \partial^2 H / \partial M^2 = 0$  yield

$$\begin{aligned} \Delta &= \frac{1}{2} T \ln [16T/(4T-1)], \\ H &= \pm T \ln \left( \frac{1-2T+(1-3T)^{1/2}}{[T(4T-1)]^{1/2}} \right) \mp (1-3T)^{1/2}, \end{aligned} \quad \frac{1}{4} \leq T \leq \frac{1}{3}.$$

These lines join together at the tricritical point  $T_c = \frac{1}{3}$ ,  $\Delta_c = \frac{2}{3} \ln 2$ , and  $H_c = 0$ . The critical values of  $H$  and  $\Delta$  go to infinity as  $T \rightarrow \frac{1}{4}$ .

Figure 4 shows the phase diagram in the  $H$ - $\Delta$  plane for various values of  $T$ . Observe that the two "wings" extending into the regions  $H < 0$  and  $H > 0$  go to infinity for  $T < \frac{1}{4}$ . They end in critical points for  $\frac{1}{3} > T > \frac{1}{4}$ , become progressively shorter with increasing temperature, and finally disappear at  $T = T_c$ . Also the angle between the wings at the tricritical point decreases to zero as  $T$  goes to  $T_c$ . In the mean-field approximation the three lines of critical points join one another continuously and with continuous slope as well.

In the vicinity of the tricritical point our molecular field theory predicts that  $(\partial x / \partial \Delta)_T$  should be perfectly finite for  $H = 0$  at all points to the right of the curve in Fig. 3, whereas to the left it diverges as  $(\Delta_c - \Delta)^{-1}$  for  $T = T_c$ . The former result appears to contradict experiment<sup>13</sup> and is quite likely an artifact of the molecular field calculation rather than a property of the Ising model itself, as is also the finite discontinuity that we find for the heat capacity  $C_x$  upon passing through  $T = T_c$  at  $x = x_c$ .

b.  $\mathcal{K} \neq 0$ . We shall discuss the whole range of values of  $\mathcal{K}/\beta$ , since the phase diagram is qualita-

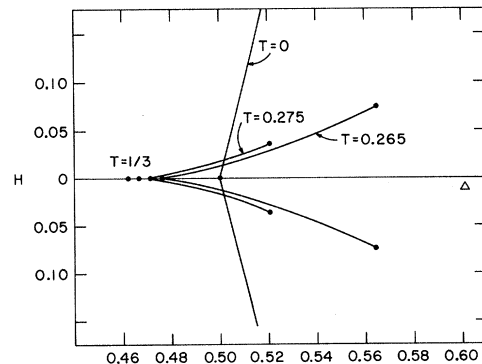


FIG. 4. Transition lines in the  $\Delta$ - $H$  plane for different values of  $T$ . For  $\frac{1}{3} > T > \frac{1}{4}$  the lines end in critical points, while for  $T < \frac{1}{4}$  they extend to infinity.

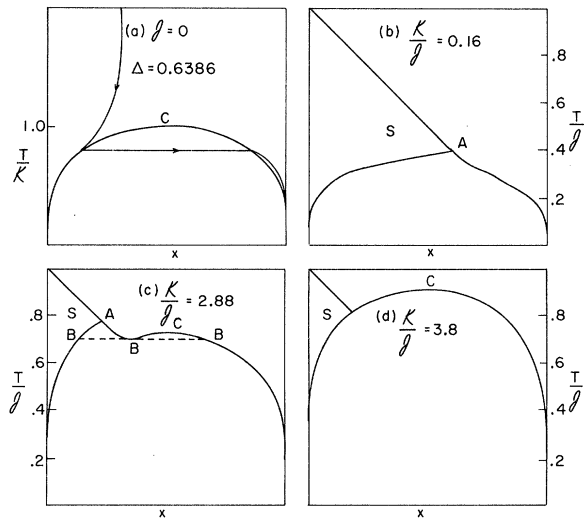


FIG. 5. Effects of nonzero  $\mathcal{K}$  on the phase diagrams. Superfluid phases are denoted by S. (a)  $\mathcal{J} = 0$ . No  $\lambda$  transition occurs in this case. Phase separation is due to interparticle interactions. The phase-separation region ends in a critical point C. A line of constant  $\Delta$  crosses the unstable region from left to right, opposite to that in Fig. 1. (b)  $\mathcal{K}/\mathcal{J} = 0.15$ . The phase diagram here is similar to that in Fig. 1. The small nonzero  $\mathcal{K}$  has caused only quantitative changes from that case. The tricritical point A has shifted to a smaller value of  $x$  and a larger value of  $T$ . (c)  $\mathcal{K}/\mathcal{J} = 2.88$ . Here features of Figs. 1 and 5(a) are both present simultaneously. There is a tricritical point A and a critical point C. In addition there is a triple point, i. e., a temperature  $T$  at which these concentrations, indicated by B, are in equilibrium. (d)  $\mathcal{K}/\mathcal{J} = 3.8$ . The value of  $\mathcal{K}$  is sufficiently large that the character of the phase diagram is predominantly that of Fig. 5(a). The  $\lambda$  line intersects the phase-separation curve below the maximum C (the critical point). There is no tricritical point in this case.

tively different in different ranges of this parameter. As discussed above, it is expected that  $\mathcal{K}/\mathcal{J}$  is small for helium mixtures and, indeed, the phase diagram for small  $\mathcal{K}/\mathcal{J}$  resembles the experimental one.

The case of  $\mathcal{J} = 0$ ,  $\mathcal{K} > 0$  has been discussed by Griffiths,<sup>10</sup> who showed that it is equivalent to a spin- $\frac{1}{2}$  Ising model with a temperature-dependent external magnetic field. The phase diagram is shown in Fig. 5(a). Phase separation occurs because the  $\text{He}^3\text{-He}^3$  and  $\text{He}^4\text{-He}^4$  interactions are more attractive than the  $\text{He}^3\text{-He}^4$  interaction. Thus there are two possible origins of phase separation. For small  $\mathcal{K}/\mathcal{J}$ , exemplified by  $\mathcal{K} = 0$ ,  $\mathcal{J} > 0$ , considered above, the superfluid transition changes from second order to first order and becomes associated with phase separation. For large  $\mathcal{K}/\mathcal{J}$ , the phase separation is a direct consequence of the interactions. For intermediate values of  $\mathcal{K}/\mathcal{J}$ , the two may be distinguished by the direction in which

the lines of constant chemical potential (constant  $\Delta$ ) cross the unstable region. In the first case they cross from right to left, as shown in Fig. 1, while, in the second, they cross from left to right as in Fig. 5(a).

For  $\mathcal{K} \neq 0$ , the point at which the  $\lambda$  line meets the phase-separation curve is given by ( $\mathcal{J} = 1$ )

$$\frac{T_c}{T_s(0)} = 1 - x_c = \frac{2\mathcal{K} + 1}{2\mathcal{K} + 3}, \quad (3.25)$$

which reduces to Eq. (3.21) for  $\mathcal{K} = 0$ . Thus, as  $\mathcal{K}/\mathcal{J}$  is increased from zero the tricritical point moves to the left, i. e., in the direction of decreasing  $\text{He}^3$  concentration [Fig. 5(b)]. As  $\mathcal{K}/\mathcal{J}$  is increased still further, the characteristics of the large  $\mathcal{K}/\mathcal{J}$  region become apparent. Thus, in Fig. 5(c), there are two maxima in the phase-separation curve, one of which corresponds to the maximum in Fig. 5(a), while the other is at the intersection of the  $\lambda$  line with the phase-separation curve. This regime is interesting because it displays a tricritical point, a critical point, and a triple point, at which three different concentrations are in equilibrium at the same temperature. Finally, as  $\mathcal{K}/\mathcal{J}$  is increased still further, the tricritical point no longer occurs, and the  $\lambda$  line merely intersects the phase-separation curve below the maximum. The phase separation is here produced by the interactions rather than by the  $\lambda$  transition. The tricritical point still appears in the theory, but it is metastable, since it occurs at a concentration where the phase separation due to interactions is absolute-

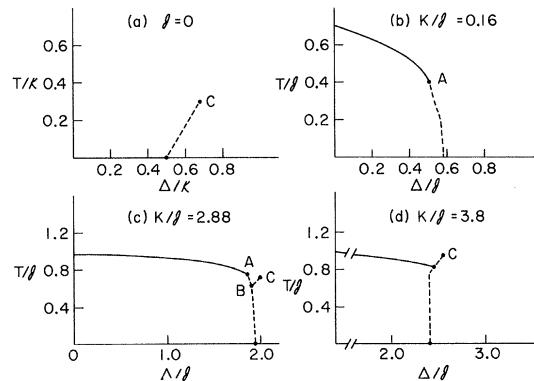


FIG. 6.  $T$ - $\Delta$  plane for the cases illustrated in Fig. 5. Second-order transitions are indicated by solid lines and first-order transitions by dashed lines. (a)  $\mathcal{K} = 0$ . The critical point is at C. (b)  $\mathcal{K}/\mathcal{J} = 0.16$ . The tricritical point is at A, separating the second-order from the first-order transitions. (c)  $\mathcal{K}/\mathcal{J} = 2.88$ . Here A is the tricritical point, B the triple point, and C the critical point. (d)  $\mathcal{K}/\mathcal{J} = 3.8$ . The tricritical point no longer appears. Only a second-order transition separates the superfluid from the normal phase. The first-order transitions separate two normal phases from one another. The critical point is at C.

ly stable.

The introduction of a nonzero  $\mathcal{K}$  does not change the conclusion that the  $\lambda$  line  $T_s(x)$  is continuous in slope with the phase-separation curve at the tricritical point. As before, this is a feature of "classical" or mean-field theories.

The phase diagrams in the  $T$ - $\Delta$  plane corresponding to the different situations shown in Fig. 3 are displayed in Fig. 6. Note that second-order transitions are distinguished from first-order transitions by the type of line employed. The second-order transitions are indicated by solid lines, and the first-order ones by dashed lines. The four examples of phase-separation diagrams shown in Figs. 5 and 6 do not correspond to the experimentally observed one. Indeed, we expect  $K \approx 0$ , so that Fig. 1 should be most nearly applicable to experiment. However, they do illustrate the variety of behavior possible for phase diagrams involving a  $\lambda$  transition.

#### IV. CONCLUSION

We have shown how a simple lattice model can explain qualitatively many of the thermodynamic properties which arise at the superfluid-normal transition in  $\text{He}^3$ - $\text{He}^4$  mixtures. Obviously, several

improvements are possible. Of particular interest are methods<sup>4</sup> of investigating the thermodynamic behavior that do not rely upon the mean-field approximation, which is well known to give incorrect information about certain details of  $\lambda$  transitions or critical points.<sup>14</sup> One can also conceive of lattice models which, following Matsubara and Matsuda,<sup>15</sup> employ quantum interactions to imitate the effects of kinetic energy and Bose statistics, and which can give rise to an order parameter having a continuous phase. Indeed, it is somewhat surprising that a model as simple as the one we have discussed bears as close a resemblance as it does to the situation observed experimentally. The agreement may be entirely fortuitous, but we would like to suppose that our approach has succeeded in including some of the essential physics.

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