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Quantum Statistics and Liquid Helium-3–Helium-4 Mixtures

The quantum statistics of Bose and Fermi manifest themselves in the behavior of liquid helium mixtures.

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All substances, when cooled down from the gaseous state and then liquefied, solidify so that they are all solids at the absolute zero of temperature. There are only two exceptions to this rule: the two helium isotopes, helium-4 and helium-3.

Helium-4, instead of becoming a solid after liquefying, shows a phase transition, at 2.2°K, to another liquid state. Keesom and Wolfke, who discovered this transition in 1928 (*1*), called this state He II, in contrast to the higher-temperature liquid state, which they called He I (*2*). This phase transition is quite different from the usual ones like condensation or solidification in that there is no latent heat—that is, there is no abrupt change in entropy *S*—nor does an abrupt change in volume *V* occur (Fig. 1). It is a more subtle transition where only abrupt changes in the temperature (*T*) derivatives of *V* and *S* occur. Thus there is a discontinuity in the thermal expansion coefficient $(1/V)(\partial V/\partial T)_P$, where *P* is pressure, as well as in the specific heat $c_V = (1/T)(\partial S/\partial T)_V$ on going through the transition. Because of the characteristic shape of a graph of the specific heat as a function of temperature near the transition point, which resembles the Greek character λ, this transition is often called a lambda transition or a second-order transition to distinguish it from the usual first-order transition (Fig. 2a).

In 1938 Kapitza (*3*) and independently Allen and Misener (*4*) discovered that the most striking difference between He I and He II was not in the equilibrium but in the nonequilibrium properties: while He I flowed through narrow tubes or capillaries like a normal fluid, He II showed "superfluid" properties in that it flowed virtually without any friction.

Helium-3 was first obtained in Los Alamos after World War II, where it became available as a by-product of nuclear reactions. At first only dilute solutions were studied, and the question was how the lambda transition of ^{4}He would be influenced by the presence of ^{3}He. In 1949 Abraham *et al.* (*5*) found that the transition temperature of a ^{4}He-^{3}He mixture at a given density decreased with increasing ^{3}He concentration *x*. Thus in the temperature-concentration (*T*-*x*) plane a line, usually called the lambda line, is traced as the locus of the transition (lambda) points for the He I-He II transition of the ^{4}He component in the ^{3}He-^{4}He mixture. It was originally thought that this lambda line would continue (*6*) until for $x = 1$ the transition temperature would be at absolute zero. However, in 1956 Walters and Fairbank (*7*) discovered that below 0.87°K, at sufficiently large ^{3}He concentrations, the homogeneous ^{3}He-^{4}He mixture becomes unstable and splits into two coexisting phases, each of which is homogeneous, but one of which has a higher concentration of ^{3}He than the other—all this in such a way, of course, that the overall amount of ^{3}He (and ^{4}He) is the same in the phase-separated mixture as in the (unstable) homogeneous mixture. This phase transition is a first-order one where abrupt changes in *S* and *V* occur. Since ^{3}He is lighter than ^{4}He, the ^{3}He-rich phase floats on top of the ^{3}He-poor one and a little meniscus or interface separating the two phases can be seen that allows one, in principle, to observe the onset of the phase separation. On the basis of this Peshkov, the discoverer of second sound (*8*)—a type of wave propagation in superfluid helium different from normal (or first) sound—was absolutely convinced that the phase separation started *under* the lambda line (*9, 10*). Thus as the temperature was decreased at first two phases would appear that would both be superfluid but with different ^{3}He concentrations, and as the temperature was further decreased the ^{3}He-rich phase would become normal; that is, the ^{4}He component of this phase would behave like a normal fluid. At absolute zero it was generally expected that the phase separation would be complete, and a pure ^{3}He phase would float on top of a pure ^{4}He phase (*10*) (Fig. 3a).

No lambda-like transition has been observed in liquid ^{3}He. This was the experimental situation around 1960, when the theoretical investigation that I want to discuss and follow began.

Helium-4 and the Ideal Bose-Einstein Gas

In this investigation I look on the phenomena in ^{3}He-^{4}He mixtures as manifestations on a macroscopic scale of the effects of quantum statistics. There are two possible quantum statistics: Bose-Einstein statistics (*11–13*) which leads, for example, to Planck's radiation law for the energy distribution as a function of frequency in the light spectrum, and Fermi-Dirac statistics (*14, 15*), which is known for instance for its importance in describing the behavior of electrons in atoms through the Pauli exclusion principle. In particular, I would like to demonstrate in a qualitative way how both these statistics manifest themselves in the behavior of the helium mixtures: How they lead to an experimental behav-

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ior of these mixtures different from that sketched above, and how this was first surmised on theoretical grounds, later confirmed experimentally, and finally led to the discovery of a new type of critical point, which is of considerable theoretical interest, as well as to the ^{3}He-^{4}He dilution refrigerator, the leading low-temperature instrument of today, which is of great practical importance. It is also interesting, from a historical point of view, to see how the actual situation repeatedly differed from the one generally expected on theoretical grounds.

To appreciate this development and the role of quantum statistics in particular in the behavior of liquid ^{3}He and ^{4}He and their mixtures, it is useful to realize that this was a continuation of a theoretical approach to the behavior of helium at low temperature that goes back to Einstein (*12*). Bose (*11*) had proposed in 1924 a way of counting the possible states of light quanta (photons) in an energy interval that led to Planck's radiation law rather than Wien's law. The latter is obtained when the classical counting procedure of Boltzmann is used. The essential difference between the two methods was that in Bose's counting the fact that all light quanta are identical was explicitly taken into account, while in Boltzmann's counting it was ignored. Einstein, deeply convinced as he was of the analogy between light and matter, immediately applied Bose's counting to the (identical) particles of an ideal gas. We say now in general that particles which obey Bose-Einstein statistics are bosons. An ideal gas of particles obeying this statistics is called an ideal Bose (or Bose-Einstein) gas.

When studying the thermodynamic properties of such an ideal Bose gas, Einstein discovered what we now call Bose-Einstein condensation. That is, a macroscopic number of gas particles "condenses" into the single-particle ground state, and since—for a very large system—a particle is essentially at rest in this ground state, a finite fraction of the particles will become "thermally inactive." The temperature T_c at which this "condensation" occurs can easily be estimated on the basis of general considerations. Bose statistics comes into force strictly when the wave packets that describe the individual gas particles start to overlap (Fig. 4); that is, when the characteristic De Broglie wavelength $\lambda(T)$ of the wave packets at temperature T is of the same order of magnitude as the average interparticle distance d.

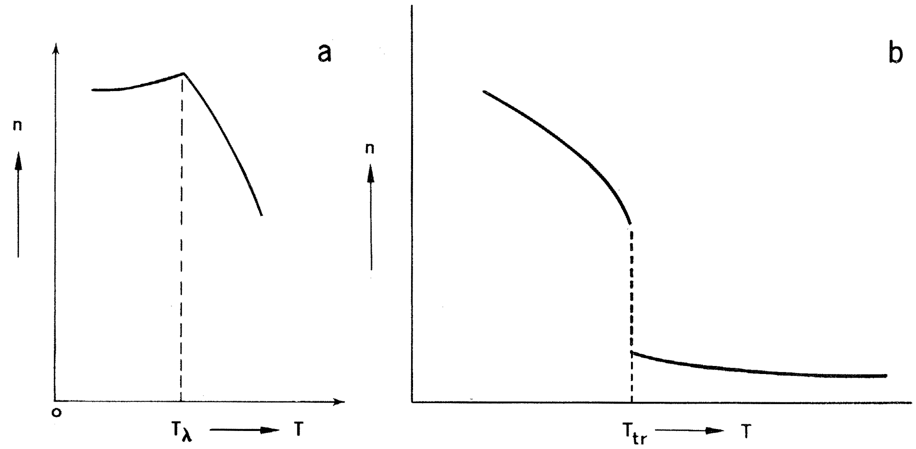

Fig. 1. Density $n = N/V$ plotted as a function of temperature T at constant pressure for (a) a second-order transition (like the lambda transition in liquid ^{4}He) where n is a continuous function of T at the transition temperature T_λ, and (b) a first-order transition (like the condensation of gaseous to liquid ^{4}He) where n is a discontinuous function of T at T_{tr}.

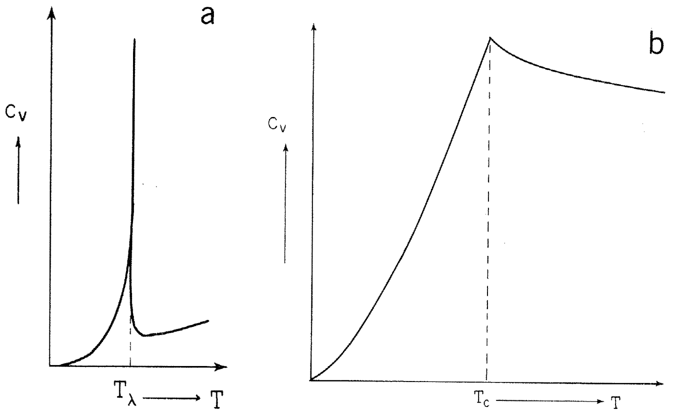

Fig. 2. Specific heat at constant volume c_V plotted as a function of the absolute temperature T for (a) ^{4}He and (b) an ideal Bose-Einstein gas. The shape of the curve in (a) resembles the Greek letter λ. In (a) T_c and in (b) T_λ is the transition temperature.

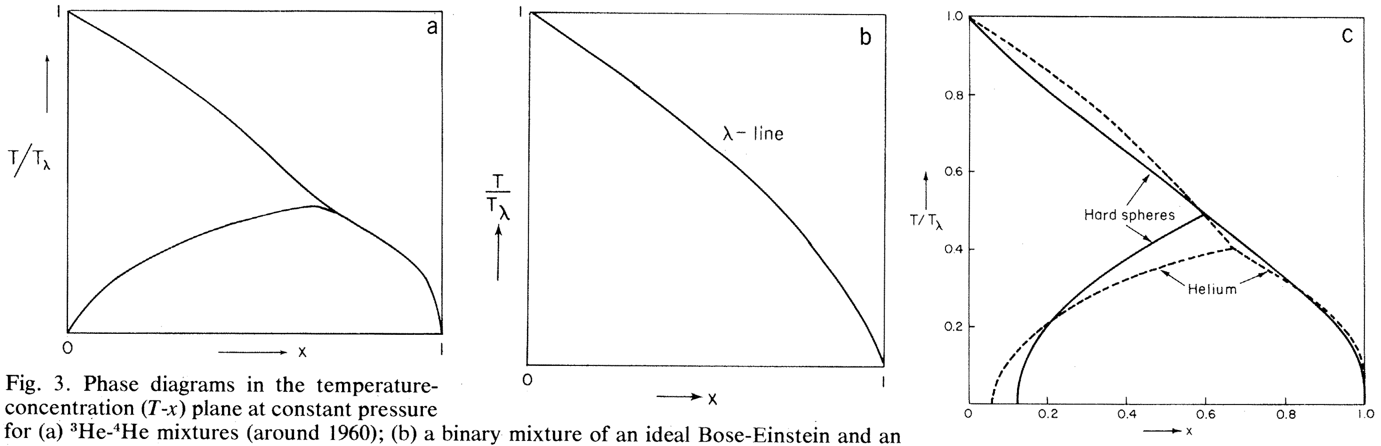

Fig. 3. Phase diagrams in the temperature-concentration (T-x) plane at constant pressure for (a) ^{3}He-^{4}He mixtures (around 1960); (b) a binary mixture of an ideal Bose-Einstein and an ideal Fermi-Dirac gas; and (c) a hard-sphere Bose-Fermi mixture at a pressure such that the density of the mixture roughly corresponds to that of ^{3}He-^{4}He mixtures (solid curve) and ^{3}He-^{4}He mixtures (present). Here T_λ is the transition temperature of the hard-sphere or helium mixtures and x is the concentration of fermions or ^{3}He, respectively.

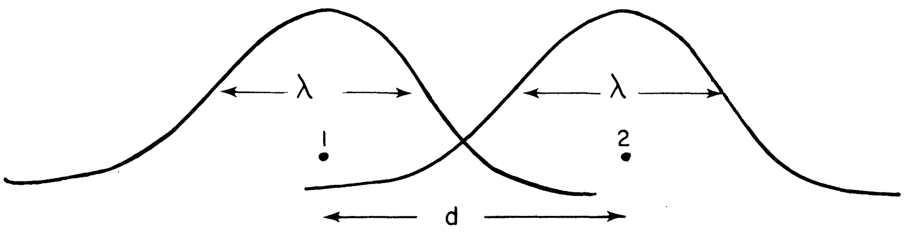

Fig. 4. Overlapping wave packets describing particles 1 and 2. The average De Broglie wavelength λ that characterizes the wave packets is of the order of the average distance d between particles.

Thus $\lambda(T_c) \equiv \lambda_c$ satisfies the simple condition $\lambda_c/d \approx 1$. Now the temperature dependence of λ can be estimated by using De Broglie's relation $\lambda = h/\bar{p}$, where $\bar{p}$ is the average momentum of the particles at temperature T and h is Planck's constant. This can also be written $\lambda \sim h/(mkT)^{1/2}$, where m is the mass of the gas particles and k is Boltzmann's constant, since $\overline{p^2}/2m = 3kT/2$ or $\overline{p^2} \simeq \bar{p}^2 \sim mkT$. Imagining the volume V divided into cubes of side d, with one particle per cube, then $Nd^3 = V$, where N is the total number of particles. Therefore $\lambda_c/d \approx n^{1/3}\lambda_c$, where $n = N/V$ is the number of particles per unit volume, so that Bose-Einstein condensation will occur in an ideal gas at a temperature determined by the relation $n\lambda_c^3 \approx 1$ [the exact relation is $n\bar{\lambda}_c^3 = 2.612$ if $\bar{\lambda}_c = h/(2\pi mkT)^{1/2}$].

Einstein also noticed that the effect of the Bose-Einstein condensation on the thermodynamic properties of the gas would be very dramatic. For instance, at fixed $T < T_c$ the pressure would remain constant for all V below a certain critical V_c instead of increasing with decreasing V. Einstein assumed that ^{4}He would follow Bose-Einstein statistics. [We would now say that ^{4}He follows Bose-Einstein statistics because it consists of an even number of elementary particles, but Einstein thought that all atoms and molecules followed Bose-Einstein statistics (*16*).] Since gaseous ^{4}He at its critical point (5.2°K) is "only" five times less dense than an ideal Bose-Einstein gas with $T_c = 5.2$°K, effects of the Bose statistics should be noticeable in the behavior of ^{4}He near its critical point in view of the dramatic nature of these quantum statistical effects. This idea was further developed by London (*17, 18*), who studied the properties of the ideal Bose-Einstein gas of particles with the same m and the same density n as liquid ^{4}He. He found $T_c = 3.13$°K, a value close to the value for the lambda transition in liquid ^{4}He. Although London realized that liquid ^{4}He was far from an ideal gas because of the strong interparticle forces between ^{4}He atoms, he argued that the quantum statistical effects in liquid ^{4}He might be so strong that in spite of these strong interparticle forces the effect of Bose-Einstein statistics would still be manifest and liquid ^{4}He might exhibit a behavior echoing in some way that of an ideal Bose-Einstein gas.

In this picture, then, the Bose-Einstein condensation temperature T_c of the ideal Bose-Einstein gas is in some way analogous to T_λ, the (lambda) transition temperature in liquid ^{4}He. In detail, the behavior of an ideal Bose gas is quite different from that of liquid ^{4}He: the specific heat does not show a lambda-like behavior near T_c and the pressure of liquid ^{4}He as a function of volume is, of course, not constant for $T < T_\lambda$ (Fig. 2b).

Helium-3–Helium-4 Mixtures and Ideal Quantum Gas Mixtures

A strong support for the idea that Bose statistics is important for understanding the properties of liquid ^{4}He—in particular for the He I-He II transition—was the fact that liquid ^{3}He showed no such transition. In order to understand this one should recall that there is another way of counting the possible states of a gas of identical particles, which differs from that of Bose. This way of counting was proposed in 1926 by Fermi (*14*) and Dirac (*15*) and is such that the particles satisfy Pauli's exclusion principle. Such particles are said to obey Fermi-Dirac statistics and are called fermions. An ideal gas of particles obeying this statistics is called an ideal Fermi (or Fermi-Dirac) gas. We now say that ^{3}He follows Fermi-Dirac statistics because it consists of an odd number of elementary particles, and has a (nuclear) spin of 1/2.

The next question is whether one can understand the lambda line or the decrease of the Bose-Einstein transition temperature $T_c(x)$ with the concentration x of the fermions in a mixture of an ideal Bose-Einstein and an ideal Fermi-Dirac gas. This was answered in the affirmative independently by Goldstein in Los Alamos in 1948 (*19, 20*) and by Heer and Daunt in 1951 (*21*). The explanation is extremely simple and follows directly from the discussion given earlier. In the mixture in volume V, Bose-Einstein condensation of the Bose component will occur when $n_B\lambda_c^3 \approx 1$, where n_B is the density of the Bose component of the mixture. But since $n_B = n(1 - x)$, where n is the overall number density of the mixture, and $\lambda_c \sim h/(mkT_c)^{1/2}$, one has immediately that $T_c(x) \sim (1 - x)^{2/3}$ or $T_c(x)/T_c(0) = (1 - x)^{2/3}$, which not only shows a decrease of T_c with x, but even agrees qualitatively with what is observed in ^{3}He-^{4}He mixtures if one identifies T_c with T_λ. It is also clear that in a mixture of an ideal Bose-Einstein gas and an ideal Fermi-Dirac gas, $T_c(x)$ will continue to decrease with increasing x until $T_c(1) = 0$ at $T = 0$°K (Fig. 3b). Thus no trace of an instability or phase separation occurs in this ideal gas mixture, and one could, of course, wonder how a phase separation could ever occur in such a mixture in view of the absence of any interaction between the two components.

Helium-4 and Helium-3 and the Hard-Sphere Quantum Gas

In order to have a chance of understanding the phase separation in liquid helium mixtures on the basis of quantum statistics, the model has to be made more realistic and at least some aspects of the interparticle forces have to be introduced.

This had been done by Bogolubov (*22*) in 1947 and in particular by Yang and Lee (*23*) in 1957, when they computed the properties of a gas of hard spheres that follow Bose statistics. Yang and Lee found that the hard-sphere Bose gas tended to differ from an ideal Bose gas in the same way as liquid ^{4}He did. While the hard-sphere Bose gas still exhibits the Bose-Einstein condensation phenomenon, it also possesses elementary excitations not like those of free (noninteracting) particles but like those of quantized sound waves (phonons). This leads to a low temperature specific heat $C_V \sim T^3$ as in liquid ^{4}He, instead of $C_V \sim T^{3/2}$ as in an ideal Bose gas. In addition, the hard-sphere Bose gas does not have a constant pressure as a function of volume for $T < T_c$.

That a hard-sphere Bose gas (or a hard-sphere Fermi gas) might be a not too bad model for liquid ^{4}He (or liquid ^{3}He) was further argued by Yang (*24*), following earlier considerations of London (*18*). The attractive part of the interparticle potential of the helium atoms is relatively weak while the repulsive part is very strong. Moreover, the interparticle distance in liquid ^{4}He and ^{3}He is relatively large; for instance, the volume of ^{4}He under its own vapor pressure is about three times as large as it would be if ^{4}He were a classical liquid because of the huge zero-point energy of the particles. As a result, the average attractive potential field in which a helium atom moves between two successive collisions, due to the repulsive part of the interparticle potential, is in first approximation a constant negative potential field, which can be ignored as far as the motion of the atoms is concerned. Thus the attractive part of the interparticle potential can in first approximation be accounted for by a constant (negative) outside potential field, which does not influence the thermal properties of the liquid at all, but only contributes to the total energy of the system. If one then in addition idealizes the repulsive part of the interparticle potential to that between hard spheres, the hard-sphere Bose (or Fermi) gas model for liquid ^{4}He (or ^{3}He) is obtained. It should be kept in mind that if one believes—as we do here—that quantum statistics plays a dominant role in the behavior of liquid ^{4}He or ^{3}He as well as their mixtures, one should compare the hard-sphere Bose or Fermi gas as well as the Bose-Fermi mixtures with the corresponding helium liquids at corresponding temperature T and (overall) density n—that is, at corresponding values of $n\lambda^3$—so that in both systems the quantum statistical effects are equally enforced.

The hard-sphere Bose-Fermi mixture studied by van Leeuwen and myself (*25–28*) in 1960 and 1961 can be described as follows. We consider N_B hard spheres that follow Bose statistics, with mass m_B, diameter a, and spin 0, and N_F hard spheres that follow Fermi-Dirac statistics, with mass m_F, the same diameter a, and spin 1/2, in a common volume V. Since the diameters of the two components of the mixture are the same, we consider an isotopic mixture. However, the derived properties of the mixture do not depend critically on this or on the value of the mass ratio $\nu = m_F/m_B$, which we take to be equal to 3/4.

In order to compute the thermodynamic properties of this mixture and in particular the phase diagram in the T-x plane ($x = N_F/N$, where $N = N_F + N_B$), we first have to find the energy eigenvalues E_j of the system, where j summarizes all quantum numbers that characterize the energy eigenstates. Then we can compute the canonical partition function $Z = \Sigma_j e^{-E_j/kT}$, from which the Helmholtz free energy $F(T, V, N_B, N_F)$ and subsequently the Gibbs free energy per particle $g(T, P, x)$ can be derived from $G(T, P, N_B, N_F)/N$. According to thermodynamics, then, the stability of the mixture for phase separation can be determined by investigating $\partial^2 g/\partial x^2$. For, if $\partial^2 g/\partial x^2 > 0$ the mixture is stable, while if $\partial^2 g/\partial x^2 < 0$ it is unstable. The properties of the coexisting phases then follow from the thermodynamic conditions of phase equilibrium—that the temperature T, pressure P, and chemical potentials μ_B and μ_F of the Bose and Fermi components in the two coexisting phases must be equal.

Table 1. Comparison of hard-sphere and helium mixtures. Symbols: T_λ is the lambda temperature at $x = 0$; T_C is the temperature and x_C the concentration of the top of the coexistence curve; $x_i(0)$ is the residual concentration of the fermions at 0°K; and α, b, and δ are constants defined in the text.

Quantity	Hard-sphere mixtures	Helium mixtures
T_C/T_λ	0.492	0.405
x_C	0.602	0.669
$x_i(0)$	0.125	0.064
αT_λ^2	3.24	1.50
$bT_\lambda^{3/2}$	0.429	3.45
δ/T_λ	0.120	0.327

The difficulty is, of course, the determination of the E_j, something that is at present completely out of reach of an exact solution. Therefore, one can at best obtain approximate eigenvalues E_j^1 and hope that they incorporate some of the most important features of the exact E_j. To find these E_j^1 one might consider applying perturbation theory, using the interparticle interaction as a perturbation on the ideal gas energy eigenvalues E_j^0, which are known. However, such a straightforward perturbation theory cannot be carried out. For, the hard-sphere gas—where the interaction prevents two particles from approaching each other closer than a—cannot be considered as a small perturbation in the sense of usual perturbation theory on an ideal gas, where there is no such restriction. However, at sufficiently low densities and temperatures, when the extension of the interparticle potential field a is small compared to both the average distance of the particles ($na^3 \ll 1$) and the average De Broglie wavelength of the particles ($a/\lambda \ll 1$), the disturbance the intermolecular potential field will cause to the free motion of the particles will be small. In that case the potential field can be considered as a small perturbation. The effect can then be taken into account in first approximation by considering the deviations of the motions of the particles in the hard-sphere gas from those in an ideal gas due to spherically symmetric (S-wave) scattering of pairs of particles. Under these conditions S-wave scattering is determined by the total scattering cross section—that is, the hard-sphere diameter a only.

This leads then to an expression $E_j^1 = E_j^0 + E_j'(a)$, where $E_j'(a)$ is the contribution to E_j^1 proportional to a. Substituting E_j^1 into the partition function Z and, for consistency, keeping no terms of higher order than a, we obtain expressions for F, G, and g that are correct to order a. These expressions differ, depending on whether the Bose component of the mixture is condensed or not. In the approximation used here the Bose-Einstein condensation of the Bose component occurs in the hard-sphere mixture at the same point as in the ideal Bose-Fermi mixture, the corrections being of higher than first order in a.

If we now investigate the stability of the mixture with respect to phase separation, we find that the mixture is stable above the Bose-Einstein transition point for all T, P, and x; that is, the mixture is always stable above the lambda line. However, we also find that below the lambda line, for densities (pressures) above a certain critical density (pressure)—where the critical density n_c is given by $n_c a^3 = (\pi/3)(\nu + 1/\nu)^{-3}$, which for $\nu = 3/4$ is ~ 1/8—the homogeneous mixture is unstable for a sufficiently low temperature and a sufficiently high fermion concentration x. This instability leads to a phase separation into two coexisting phases, one of which is relatively rich in fermions and has a normal (not condensed) Bose component, while the other is relatively rich in bosons and has a superfluid (condensed) Bose component. The critical point for this phase separation at a given $P > P_c$—that is, the point in the T-x plane where the phase separation starts—is situated on the lambda line. Decreasing the temperature (keeping P constant) leads to an increasing concentration difference between the two coexisting phases. At the absolute zero of temperature the phase separation remains incomplete, however, for all pressures $P > P_c$. That is, at 0°K a pure ^{3}He phase coexists with a ^{3}He-^{4}He mixture. It is interesting to note that while the occurrence of phase separation is intimately connected with the Bose-Einstein condensation of the Bose component of the mixture, the incomplete phase separation at 0°K is due to the Fermi-Dirac statistics of the Fermi component. A mixture of two hard-sphere Bose gases, or of a hard-sphere Bose gas with a hard-sphere gas following Boltzmann's statistics, would show a complete phase separation at 0°K.

A phase diagram for the hard-sphere Fermi-Bose mixture at a density comparable to that found in helium mixtures (where $na^3 \approx 0.365$) is drawn in Fig. 3c, showing a solubility of the fermions in the bosons at 0°K of about 12.5 percent. It will be clear that this phase diagram differs from the one in Fig. 3a in at least two important aspects: the critical point for the phase separation is on the lambda line, and the phase separation remains incomplete at 0°K. All attempts to remedy this difference failed since one can show, for instance, that the theoretical model—at least in the approximation used—will never lead to a critical point below the lambda line, but always to one on the lambda line.

A solution to this dilemma came when Edwards *et al.* (*29*) in 1965, guided independently by experimental indications (*30*), discovered the incomplete phase separation of helium mixtures, with a limiting solubility of ^{3}He in ^{4}He at 0°K of about 6.4 percent. Also, in 1967, Graf *et al.* (*31*) discovered that for the helium mixtures the critical point for the phase separation is on the lambda line, with a location in the T-x plane that is not too different from that for the hard-sphere Bose-Fermi mixtures at comparable density.

A closer comparison of the phase diagrams of the helium and hard-sphere mixtures reveals that they are—with one exception—qualitatively the same (Fig. 3c). The coexistence curve, or locus of coexisting phase points in the T-x plane, approaches the critical point for phase separation linearly, both for helium mixtures and for hard-sphere Bose-Fermi mixtures. However, the slope of the lambda line and that of the outer branch of the coexistence curve, $x_0(T)$, at the critical point for phase separation are not the same for helium mixtures, while they are the same for the theoretical curve. This equality of slope is probably not really true for the hard-sphere Bose-Fermi mixture, but only a consequence of the approximations used in evaluating the partition function Z. The behavior of the coexistence curve near 0°K is the same for the helium and hard-sphere mixtures: the outer branch behaves like $x_0(T) = 1 - bT^{3/2}e^{-\delta/T}$, while the inner branch $x_i(T)$ behaves like $x_i(T) = x_i(0) + \alpha T^2$. The constants b, δ, and α are independent of x and T and depend only on P. The expression for $x_0(T)$ is a direct consequence of the equality of the chemical potentials of the Bose components in the two coexisting phases; the temperature dependence is due to the Bose statistics. The expression for $x_i(T)$ follows from the equality of the chemical potentials of the Fermi components in the two coexisting phases; the quadratic behavior of $x_i(T)$ as a function of T is due to the Fermi-Dirac statistics. A comparison of numerical values for the experimental and theoretical phase diagrams is given in Table 1, which shows that the agreement is semiquantitative.

Concluding Remarks

1) At the critical point of the phase separation two phases become identical, namely the ^{3}He (fermion)-rich normal phase and the ^{4}He (boson)-rich superfluid phase. This is similar to the situation at the critical point for condensation, where the gas and liquid phases become identical, or at the critical point for phase separation in a classical binary mixture such as phenol and water (Fig. 4a), where the phenol-rich and phenol-poor phases become identical. But the environment of the critical point in helium mixtures is quite different from that found in classical binary mixtures: while the approach of the two branches of the coexistence curve to the critical point in a classical binary mixture is approximately cubic (*32*), it is linear here (*31*) (Fig. 5). In addition, there is in this case a third line meeting the coexistence curve at the critical point: the lambda line. Therefore, this critical point has something of the character of a triple point, where three lines also meet. One could call it a tricritical point, emphasizing its difference from a "normal" critical point, and one could say that at the tricritical point a second-order (lambda) phase transition goes over into a first-order transition. Such a point has also been found in phase diagrams for other systems—for example, in the temperature-magnetization diagram of certain highly anisotropic antiferromagnets like $FeCl_2$. A more detailed comparison of the behavior of the helium and the hard-sphere mixtures near the tricritical point reveals a general similarity with differences in detail, which might be due to the approximations used in the evaluation of Z for the hard-sphere mixture (*27*).

The critical point for phase separation remains on the lambda line for all $P > P_c$ in the hard-sphere mixtures. This is in agreement with what has recently been found by Johnson (*33*) and Lai (*34*) for the helium mixtures, at least up to about 20 atmospheres. Therefore, there seems to be no indication that at any pressure $P > P_c$ the liquid helium mixtures would behave as in Fig. 3a; they always show a tricritical point. There are indications that a critical point such as that in Fig. 3a might occur in the class of antiferromagnets mentioned above (*27*).

The more detailed behavior as a function of pressure is not the same, however, in the helium and hard-sphere mixtures, neither near the tricritical point nor near 0°K. This is probably due to the very incomplete incorporation of the attractive part of the interparticle potential in the model.

2) The incomplete phase separation at the absolute zero of temperature is the basis for the ^{3}He-^{4}He dilution refrigerator. In this refrigerator, ^{3}He is pumped off from the lower (^{3}He-poor) mixture, which will then be replenished from the

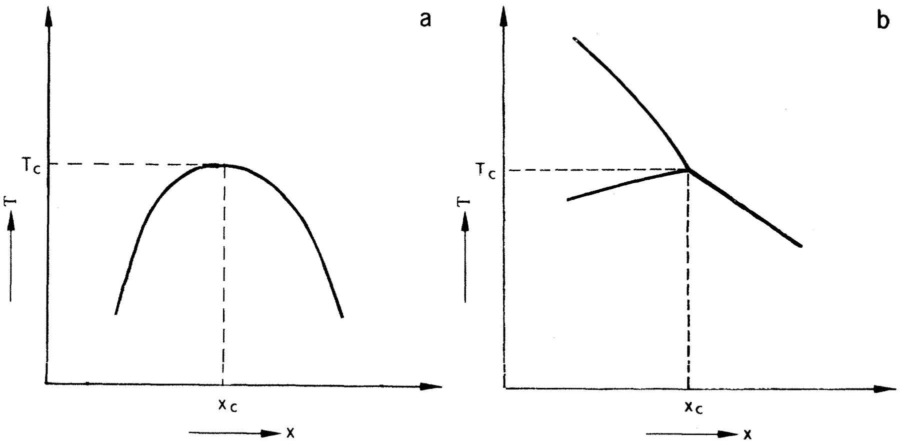

Fig. 5. Behavior near the critical point for phase separation for (a) an ordinary binary mixture (like phenol and water) and (b) ^{3}He-^{4}He mixtures. The neighborhood of the critical point is described in (a) approximately by a cubic equation $|T - T_c| \sim |x - x_c|^3$ and in (b) by a linear equation $|T - T_c| \sim |x - x_c|$. Also, in (b) three lines join in the critical point: the lambda line and the two branches of the coexistence curve. This point is now called a tricritical point.

upper (^{3}He-rich) mixture (Fig. 6). It will be predominantly the more energetic ^{3}He atoms in the upper mixture that will replenish the lower mixture, since a ^{3}He atom has to do work to transfer from the upper to the lower mixture. Consequently, the more energetic ^{3}He atoms will be pumped off, while the less energetic ^{3}He atoms stay behind. In other words, the mixtures will cool off. By reintroducing the pumped-off ^{3}He again in the upper mixture, a continuously operating machine can be constructed that can maintain temperatures of about 0.015°K and less for extended periods of time (of the order of weeks) (*35*). The importance of the incomplete phase separation at 0°K will be appreciated if one realizes that if there were complete phase separation at 0°K, the ^{3}He concentration in the lower mixture would decrease to zero with the temperature and a temperature of "only" about 0.3°K could be maintained.

3) Near 0°K it is possible to calculate F and G to higher order in a, in fact to order $a^{5/2}$, by using improved perturbed energy levels E_j^1 (*26*, *28*). In that case the phonon excitations of the Bose component are taken into account, which was not the case in the earlier calculation. This higher-order calculation confirms not only the existence of a phase separation—in fact, the value of the critical density for this to occur decreases, so that the tendency for phase separation is enhanced—but also the behavior of $x_0(T)$ and $x_i(T)$ near 0°K as quoted above.

Such a calculation also suggests the possibility, in principle, of yet another phenomenon in the hard-sphere Bose-Fermi mixtures, and thus perhaps in the helium mixtures, due to the quantum statistics. This phenomenon, which we called supermobility (*28*), is the formation of bound pairs of fermions at a sufficiently low fermion concentration and temperature. This process is similar to the condensation of electrons into pairs—so-called Cooper pairs—in a superconductor. The fermion pairs would then move without friction through the mixture under the influence of a (fermion) concentration gradient, just as (Cooper) pairs of electrons move without resistance in a superconductor under the influence of an electric field. A phase transition from a thermodynamic state where the fermions in the mixture are not paired to a thermodynamic state where they are paired could, in principle, be observed by a little peak in the specific heat or a singularity in the magnetic susceptibility. A much more realistic discussion of this phenomenon as well as of other aspects of the very low temperature part of the phase diagram (below 0.4°K) has been given by Bardeen *et al.* (*36*) on the basis of a semiphenomenological model for the helium mixtures (*37*).

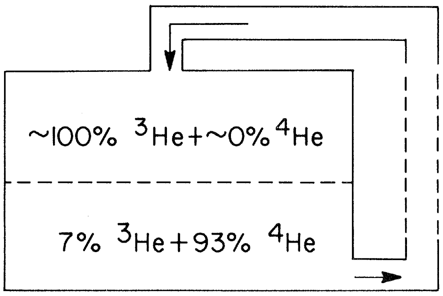

Fig. 6. Principle of the ^{3}He-^{4}He dilution refrigerator. The ^{3}He, pumped out of the lower mixture, is replenished from the upper mixture. By reintroducing the ^{3}He again in the upper mixture a continuously working machine is obtained. The dotted lines indicate the left out parts of the refrigerator.

Summary

I have argued, following Einstein and London, that Bose-Einstein statistics is important for understanding the behavior of superfluid ^{4}He, while Fermi-Dirac statistics is important for understanding that of ^{3}He. In order to understand qualitatively the general behavior of ^{3}He-^{4}He mixtures at constant pressure, the interaction between the helium atoms cannot be neglected. A very simple model of ^{3}He-^{4}He mixtures is then a binary mixture of two kinds of hard spheres that follow Bose-Einstein and Fermi-Dirac statistics, respectively. This model correctly predicts the most striking features of the phase diagrams of helium mixtures in the temperature-concentration plane. In particular, the Bose-Einstein statistics of ^{4}He is responsible for the occurrence of a phase separation of the mixture at low temperatures that starts at an unusual type of critical point, while the Fermi-Dirac statistics of ^{3}He leads to an incomplete phase separation near the absolute zero of temperature, which makes possible the successful operation of a powerful cooling device, the helium dilution refrigerator.

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38. I thank Professor S. A. Goudsmit for helpful comments.