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Phase Separation in Isotopic Fermi-Bose Mixtures

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An isotopic mixture of fermions and bosons has been investigated at a given pressure, using the hard sphere diameter a as a perturbation parameter. The results agree with those obtained before at a given density. To first order in a it is found that above a critical pressure the mixture separates into two coexisting phases. The phase separation curve has its top on the λ curve of the mixture. The phase separation remains incomplete at $T = 0$ for a wide range of densities. The slopes at the top and the behavior near $T = 0$ of the phase separation curve have been computed. Also the osmotic pressure of dilute solutions has been obtained.

I. INTRODUCTION

Motivated by Walters and Fairbank' s[1] experimental discovery of the phase separation (p. s.) in He^3–He^4 mixtures, as well as by a remark of Uhlenbecks[2] and by the success of Huang, Yang, and Lee[3] in explaining qualitatively some of the most striking properties of pure He^4 on the basis of a hard-sphere Bose gas, we investigated in two previous publications the properties of isotopic hard-sphere Fermi-Bose mixtures. The hope was that a study of such mixtures would lead to a qualitative understanding of He mixtures. In these papers,[4,7] a first-order calculation in the hard-sphere diameter a was carried out at fixed density, which predicted (1) a phase separation of the mixture, which remained incomplete at $T = {}^\circ$K for He densities and (2) the top of the phase-separation curve to be *on* the λ curve of the mixture. These predictions were later confirmed for

He mixtures by Edwards *et al.* and Graf. Lee, and Reppy,[6] respectively.

In the second paper[7] a higher-order calculation in a was carried out at $T=0$. This lead to the prediction of the possibility of "superfluidity" of the Fermi component in the Bose component. The critical temperature for this to occur, however, was extremely low.

Recently Bardeen, Baym, and Pines[8] discussed the phase separation as well as the superfluidity in dilute He mixtures in the neighborhood of $T=0$ in a different fashion, by determining the effective interaction between He^3 atoms in these dilute solutions.

In this paper we present a modified and extended version of the calculations made in the first publication[4]: The mixture is studied now at a fixed external pressure $\underline{p}$ instead of at a fixed density.[9] Although the two treatments are different, they lead to qualitatively identical results. This may also be viewed as an *a posteriori* justification of the earlier calculations at constant density, which were simpler but involved unfamiliar coexistence conditions.[10]

The model studied consists of a mixture of N_F hard-sphere fermions with diameter a, mass m_F and spin $\frac{1}{2}$ obeying therefore Fermi statistics and of N_B hard-sphere bosons with diameter a, mass m_B and spin 0, obeying therefore Bose statistics. The total number of particles $N=N_F+N_B$ is fixed; and if the volume is V, then the total number density n, the number densities n_F and n_B of the Fermi and the Bose component, respectively, and the concentration x of the Fermi component are given by

$$n=N/V, n_F=N_F/V, \quad n_B=N_B/V, \quad x=N_F/N\,.$$

The calculations are based on the pseudopotential method of Huang, Yang, and Lee,[3] which leads most directly to expressions for the thermodynamic quantities of the mixture to first order in $\underline{a}$.

The Hamiltonian of the system is given by

$$\mathcal{H}=-\sum_{i=1}^{N_F}\frac{\hbar^2\nabla_i^2}{2m_F}-\sum_{j=1}^{N_B}\frac{\hbar^2\nabla_j^2}{2m_B}$$
$$+\frac{1}{2}\sum_{i\neq i'}^{N_F}\phi_{FF}(\vec{r}_i-\vec{r}_{i'})+\sum_{i=1}^{N_F}\sum_{j=1}^{N_B}\phi_{FB}(\vec{r}_i-\vec{r}_j).$$
$$+\frac{1}{2}\sum_{j\neq j'}^{N_B}\phi_{BB}(\vec{r}_j-\vec{r}_{j'}). \tag{1.2}$$

Here the pseudopotentials $\phi_{IJ}(\vec{r})$ are given by

$$\phi_{IJ}(\vec{r})=\phi_{IJ}\delta(\vec{r}) \quad (I,J=F,B) \tag{1.3a}$$

with

$$\phi_{IJ}=2\pi a\hbar^2(m_I^{-1}+m_J^{-1}) \quad (I,J=F,B). \tag{1.3b}$$

Although one could also easily consider the case where the hard-sphere diameters (or scattering lengths) of the three interactions $\phi_{IJ}(I,J=F,B)$ are different, we have restricted ourselves to the case of equal $\underline{a}$ for all three types of the interactions.

The possibility of an instability, leading to a phase separation in the mixture, is investigated by considering the Gibbs free energy $\mathcal{G}$, defined by

$$\mathcal{G}=Ng(x,T,p)=F+pV$$
$$=N[x\mu_F(x,T,p)+(1-x)\mu_B(x,T,p)]\,, \tag{1.4}$$

where g is the Gibbs free energy per particle. It proved convenient to calculate first the Helmboltz free energy F and then g from the chemical potentials

$$\mu_I=(\partial F/\partial N_I)_{V_F T}(I=F,B)$$

and the last relation of (1.4).

A phase separation of the mixture at given T and p is then related to an instability domain in which

$$\partial^2 g(x,T,p)/\partial x^2<0 \tag{1.5}$$

as a function of x. The concentrations x_l and x_u of the two coexisting phases at a given p and T are found in our calculations from a bitangent construction to $g(x,T,p)$ or equivalently from the equality of the chemical potentials of the Fermi and Bose components in the two phases, namely,

$$\mu_F(x_l(T,p),T,p)=\mu_F(x_u(T,p),T,p),$$
$$\mu_B(x_l(T,p),T,p)=\mu_B(x_u(T,p),T,p). \tag{1.6}$$

The p.s. curve at a given pressure p is the locus of all coexisting points (x_l, x_u) for varying T, i.e., of all solutions of the Eqs. (1.6), in the (x,T) plane. The concentrations x_l and x_u of the coexisting phases will be computed as a function of the reduced temperature $T^*=T/T_\lambda$ (T_λ is the λ temperature of the pure Bose component) and the reduced pressure $p^*=2\pi m_B a^5 h^{-2} p$, and the results depend only on the mass ratio $\nu=m_F/m_B$. As we will see, this dependence is fairly weak in the neighborhood of the value of interest, $\nu=\frac{3}{4}$. We will set $\nu=\frac{3}{4}$ in all the calculations. p^* here plays the role played by the reduced density in the earlier calculations.[4,7]

We first discuss in Sec. 2 the thermodynamic properties of the mixture at $T=0$, which can all be derived from the ground-state energy of the mixture. In Sec. 3 the discussion is extended to finite temperatures and the location of the top of the p.s. curve is computed. In Sec. 4 further details of the p.s. curve are given: the slopes of the curve at the top and the behavior of the curve in the neighborhood of $T=0$.

One of the main differences between the hard sphere and the He mixtures is that, because of the large thermal expansion of the hard-sphere mixture, the density of this mixture varies considerably with T at constant p, whereas that of He mixtures stays practically constant. Therefore, we have studied in Sec. 5 a hard-sphere mixture under an external pressure $p(T)$, which varies with T in such a way that the density of the pure Bose component remains for all T the same as it is for $T=0$. In this way the density of the mixture varies considerably less than when the external pressure is kept constant.

In Sec. 6 a number of points a. o. the influence of the excitation spectrum of the Bose component on the results obtained, the osmotic pressure, and the connection between the hard sphere and the He mixtures are discussed.

II. PHASE SEPARATION AT $T = 0$

At $T=0$ all the thermodynamic properties of the mixture can be derived from the ground-state energy E, which equals then the Helmholtz free energy F.

The ground-state energy E of the mixture can be obtained, to first order in a, by a direct generalization of the existing calculations[3,9] for the pure components, yielding the following expressions for E (or F):

$$F(N_F, N_B, V, 0) = E(N_F, N_B, V) = F_F{}^0 + F_B{}^0 + F_{\text{int}}, \tag{2.1a}$$

where $F_F{}^0 = E_F{}^0 = \frac{3}{5} N_F (h^2/8m_F)(3N_F/\pi V)^{2/3}$, (2.1b)

$$F_B{}^0 = E_B{}^0 = 0, \tag{2.1c}$$

$$F_{\text{int}} = E_{\text{int}} = (2V)^{-1}(\tfrac{1}{2}\phi_{FF} N_F{}^2 + 2\phi_{FB} N_F N_B + \phi_{BB} N_B{}^2). \tag{2.1d}$$

Here $E_F{}^0$ is the ground-state energy of an ideal Fermi gas, $E_B{}^0$ is that of an ideal Bose gas, while E_{int}, the contribution to E of the hard-sphere interaction, consists of three terms: viz. the contribution due to Fermi-Fermi, Fermi-Bose, and Bose-Bose interactions, respectively. The different numerical factors in front of the three interaction terms are due to different statistics.

All thermodynamic functions of interest can be derived from (2.1a) by differentiation. In particular, one finds for the chemical potentials μ_F and μ_B, respectively,

$$\mu_F = \left(\frac{\partial F}{\partial N_F}\right)_{N_B, V, T} = \frac{h^2}{8m_F}\left(\frac{3xn}{\pi}\right)^{2/3} + [\tfrac{1}{2}\phi_{FF}x + \phi_{FB}(1-x)]n,$$

$$\mu_B = \left(\frac{\partial F}{\partial N_B}\right)_{N_F, V, T} = [\phi_{FB}x + \phi_{BB}(1-x)]n, \tag{2.2}$$

while the pressure p is given by

$$p = -\left(\frac{\partial F}{\partial V}\right)_{N_F, N_B, T} = \frac{2}{5}\frac{h^2}{8m_F}\left(\frac{3}{\pi}\right)^{2/3}(xn)^{5/3} + [\tfrac{1}{4}\phi_{FF}x^2 + \phi_{FB}x(1-x) + \tfrac{1}{2}\phi_{BB}(1-x)^2]\, n^2. \tag{2.3}$$

To obtain the Gibbs free energy per particle, g, as a function of x and p, one uses (1.4) and (2.2) and solves for n as a function of x and p from (2.3).

In order to investigate the stability of the mixture at $T=0$, we compute $\partial^2 g(x, o, p)/\partial x^2$. Using the Gibbs-Duhem relation,

$$x\left(\frac{\partial \mu_F}{\partial x}\right)_{T,p} + (1-x)\left(\frac{\partial \mu_B}{\partial x}\right)_{T,p} = 0, \tag{2.4}$$

one has

$$\frac{\partial g(x, T, p)}{\partial x} = \mu_F(x, T, p) - \mu_B(x, T, p) \tag{2.5}$$

and
$$\frac{\partial^2 g(x, T, p)}{\partial x^2} = \frac{1}{1-x}\frac{\partial \mu_F(x, T, p)}{\partial x} = -\frac{1}{x}\frac{\partial \mu_B(x, T, p)}{\partial x} \tag{2.6}$$

Calculating the derivatives on the right-hand side of (2.6) and using (2.2) and (2.3), one finds

$$\frac{\partial^2 g(x,0,p)}{\partial x^2} = n\left(\frac{h^2}{4m_F}\frac{\phi_{BB}}{(3\pi^2 xn)^{1/3}} + \tfrac{1}{2}\phi_{FF}\phi_{BB} - \phi_{FB}{}^2\right) \times\left(\frac{h^2}{4m_F}\frac{x^2}{(3\pi^2 xn)^{1/3}} + \tfrac{1}{2}\phi_{FF}x^2 + 2\phi_{FB}x(1-x) + \phi_{BB}(1-x)^2\right)^{-1}$$
$$= \frac{2na\nu}{\pi}\frac{(\pi/24xna^3)^{1/3} - \frac{1}{2}(\nu+\nu^{-1})}{(\pi/24xna^3)^{1/3}x^2 + 2x - x^2 + 2\nu(1-x)}. \tag{2.7}$$

Thus one sees that the mixture will be unstable when

$$xna^3 > \tfrac{1}{3}\pi(\nu+\nu^{-1})^{-3}, \quad \nu = m_F/m_B, \tag{2.8}$$

since for such densities and concentrations $\partial^2 g(x,0,p)/\partial x^2 < 0$. To see the implications of this condition in the (x,p) plane one needs n as a function of x and p. For $p=0$, the condition (2.8) cannot be fulfilled, since $n(x,0,0)=0$ for any x between 0 and 1. As it follows from (2.3), that $xn(x,0,p)$ is an increasing function of both x and p, upon increasing p a critical value p_c of p will be reached for $x=1$, for which

$$n(1,0,p_c)a^3 = \tfrac{1}{3}\pi(\nu+\nu^{-1})^{-3}. \tag{2.9}$$

For $p > p_c$ there will be a domain of values $x_i \leq x \leq 1$ for which (2.8) is satisfied, where x_i is the lowest value of x for which (2.8) is satisfied. The value of p_C can be found by substituting $n(1,0,p_C)$ from (2. 9) for n in (2. 3). One obtains

$$p_C = \frac{h^2}{2\pi m_B a^5} p_C{}^* = \frac{h^2}{2\pi m_B a^5} \frac{4\pi}{3\nu} \frac{1+\frac{3}{5}(\nu+\nu^{-1})}{(\nu+\nu^{-1})^6} . \tag{2.10}$$

For $\nu = \frac{3}{4}$ one has $p_C{}^* = 0.02012$, which corresponds to $p_C = 1.91$ atm if one takes $a = 2.556$ Å and $m_B = m_{\mathrm{He}}$.[4]

As a consequence of this instability of the mixture, a phase separation develops in the mixture for $p > p_C$, starting at the value $x = 1$ for $p = p_C$.

Since the coexisting phases $x_l(T,p)$ and $x_u(T,p)$ lie outside the instability domain, it follows from the above that $x_u(0,p) = 1$ for $T = 0$. The other phase $x_l(0,p)$ can then be found from the first equation (1. 6)[11]:

$$\mu_F(x_l(0,p),0,p) = \mu_F(1,0,p). \tag{2.11}$$

The function $x_l(0,p)$ has been calculated with (2. 2) and (2. 3) from (2. 11) as a function of p^* and is plotted in Fig. 1. We note that $x_l(0,p) \neq 0$ for all $p < p_{\max}$[12] so that the phase separation is incomplete at $T = 0$ for such pressures.

The phase separation of the mixture at $T = 0$ for $p > p_C$ found in this section is primarily a consequence of the interaction or more precisely of the particular form of the interaction term due to the statistics of the two components.[13] Although the mass ratio appears in the formulas, the dependence of the results on ν is weak as long as ν does not differ too much from 1.

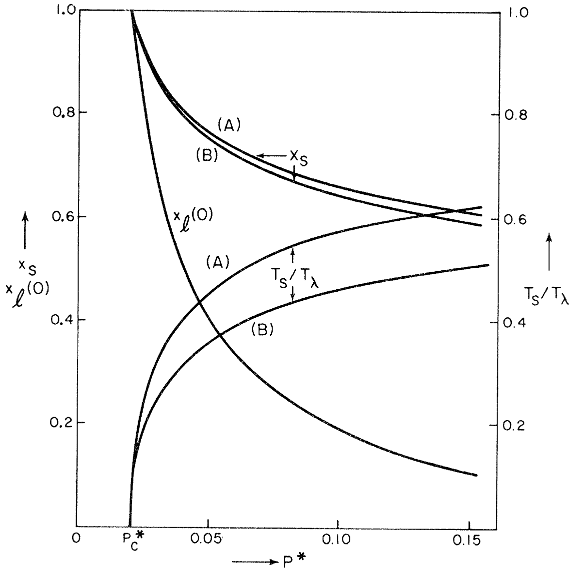

FIG. 1. $x_l(0)$, x_S and T_S/T_λ as a function of $p^* = 2\pi m_B a^5 h^{-2} p$. Case (A), constant external pressure; case (B), temperature-dependent external pressure (Sec. 5). He densities correspond to $0.10 \lesssim p \lesssim 0.13$.

III. PHASE SEPARATION FOR $T > 0$

At temperatures $T > 0$ the computation of the thermodynamic quantities F, g, etc., of the mixture is complicated by the λ phenomenon. To lowest order in a, the λ temperature of the mixture as a function of x and n is the same as that in an ideal Fermi-Bose mixture, so that the λ curve of the hard-sphere mixture is still determined by the ideal gas formulas.[14] We now summarize the relevant formulas for later use.

The unperturbed (i. e., ideal gas) chemical potentials $\mu_F{}^0$ and $\mu_B{}^0$ are given in terms of the number density n and the concentration x by

$$xn = -2\lambda_F{}^{-3} G_{\frac{3}{2}}(-\exp\beta\mu_F{}^0), \tag{3.1}$$

$$(1-x)n = \lambda_B{}^{-3} G_{\frac{3}{2}}(\exp\beta\mu_B{}^0), \quad T > T_\lambda(x,p). \tag{3.2}$$

Here λ_I $(I = F, B)$, the thermal wavelength of a particle, is given by

$$\lambda_I{}^2 = h^2/2\pi m_I kT \quad (I = F, B). \tag{3.3}$$

The function $G_\alpha(z)$ is defined by the integral

$$G_\alpha(z) = [1/\Gamma(\alpha)] \int_0^\infty dt\, t^{\alpha-1} z e^{-t}/(1 - z e^{-t}). \tag{3.4}$$

The formula (3. 2) for $\mu_B{}^0$ only holds for temperatures T above the λ temperature $T_\lambda(x,p)$ of the mixture at given x and p. The λ curve of the mixture, $T_\lambda(x,p)$, follows from the condition that $\mu_B{}^0 = 0$ for $T = T_\lambda(x,p)$ i.e., from the equation

$$(1-x)n[x, T_\lambda(x,p), p] = \lambda_B{}^{-3} G_{\frac{3}{2}}(1) = 2.612\lambda_B{}^{-3}. \tag{3.5a}$$

Although the precise dependence of $T_\lambda(x,p)$ on x and p is rather complicated, because n is a complicated function of x, T, and p, $T_\lambda(x,p)$ behaves roughly as $T_\lambda(x,p) \cong T_\lambda(o,p)(1-x)^{2/3}$ as in an ideal gas mixture at constant density. For temperatures T below $T_\lambda(x,p)$ the fraction ξ of the Bose particles which occupy the zero-momentum state becomes finite and (3. 2) has to be replaced by

$$(1-x)n(1-\xi)=\lambda_B^{-3}\,G_{\frac{3}{2}}(1),\quad T<T_\lambda(x,p)\,. \tag{3.5b}$$

In the following it will be understood in formulas involving ξ or $\mu_B{}^0$ that $\mu_B{}^0=0$ for $T<T_\lambda(x,p)$ while $\xi=0$ for $T>T_\lambda(x,p)$.

We are now in a position to write down the Helmholtz free energy F of the mixture to first order in a for $T>0$[3,15,16]:

$$F(N_F,N_B,V,T)=F_F{}^0+F_B{}^0+F_{\text{int}}, \tag{3.6a}$$

where $$F_F{}^0(N_F,V,T)=N_F\mu_F{}^0+2VkT\lambda_F{}^{-3}\,G_{\frac{5}{2}}(-\exp\beta\mu_F{}^0), \tag{3.6b}$$

$$F_B{}^0(N_B,V,T)=N_B\mu_B{}^0-VkT\lambda_B{}^{-3}\,G_{\frac{5}{2}}(\exp\beta\mu_B{}^0), \tag{3.6c}$$

$$F_{\text{int}}(N_F,N_B,V,T)=(1/2V)[\tfrac{1}{2}\,\phi_{FF}N_F{}^2+2\phi_{FB}N_FN_B+\phi_{BB}N_B{}^2(2-\xi^2)]\,. \tag{3.6d}$$

Here $F_F{}^0$ is the free energy of an ideal Fermi gas, and $F_B{}^0$ is that of an ideal Bose gas, while F_{int} is the contribution of the hard-sphere interaction to the free energy. Equations (3.6c) and (3.6d) apply to both regions $T\gtrless T_\lambda(x,p)$, provided that $\mu_B{}^0$ and ξ are taken as explained above.

The chemical potentials μ_F and μ_B follow from (3.6a)

$$\begin{aligned}\mu_F&=\left(\frac{\partial F}{\partial N_F}\right)_{N_B,\,V,\,T}=\mu_F{}^0+[\tfrac{1}{2}\,x\phi_{FF}+(1-x)\phi_{FB}]n,\\ \mu_B&=\left(\frac{\partial F}{\partial N_B}\right)_{N_F,\,V,\,T}=\mu_B{}^0+[x\phi_{FB}+(1-x)(2-\xi)\phi_{BB}]n,\end{aligned} \tag{3.7}$$

while the pressure p is given by

$$\begin{aligned}p=-\left(\frac{\partial F}{\partial V}\right)_{N_F,\,N_B,\,T}&=-2kT\lambda_F{}^{-3}\,G_{\frac{5}{2}}(-\exp\beta\mu_F{}^0)+kT\lambda_B{}^{-3}\,G_{\frac{5}{2}}(\exp\beta\mu_B{}^0)\\ &\quad+\{\tfrac{1}{4}\,\phi_{FF}x^2+\phi_{FB}x(1-x)+\tfrac{1}{2}\,\phi_{BB}(1-x)^2[1+(1-\xi)^2]\}n^2.\end{aligned} \tag{3.8}$$

To investigate the stability of the mixture we need the Gibbs free energy per particle g as a function of x, T, and p. This can be achieved in an analogous manner as in Sec. 2, with the help of the Eqs. (1.4), (3.7), (3.8), (3.1), (3.2), and (3.5b). For the second derivative $\partial^2 g(x,T,p)/\partial x^2$ one finds different expressions depending on whether $T>T_\lambda(x,p)$ or $T<T_\lambda(x,p)$, namely

$$\frac{\partial^2 g(x,T,p)}{\partial x^2}=n\,\frac{\left(\dfrac{\partial\mu_B{}^0}{\partial n_B}\right)_T\left(\dfrac{\partial\mu_F{}^0}{\partial n_F}\right)_T+\dfrac{1}{2}\,\phi_{FF}\left(\dfrac{\partial\mu_B{}^0}{\partial n_B}\right)_T+2\phi_{BB}\left(\dfrac{\partial\mu_F{}^0}{\partial n_F}\right)_T+\phi_{FF}\phi_{BB}-\phi_{FB}{}^2}{(1-x)^2\left(\dfrac{\partial\mu_B{}^0}{\partial n_B}\right)_T+x^2\left(\dfrac{\partial\mu_F{}^0}{\partial n_F}\right)_T+\tfrac{1}{2}\phi_{FF}x^2+2\phi_{FB}x(1-x)+2\phi_{BB}(1-x)^2},\quad T>T_\lambda(x,p), \tag{3.9}$$

$$\frac{\partial^2 g(x,T,p)}{\partial x^2}=n\,\frac{\phi_{BB}\left(\dfrac{\partial\mu_F{}^0}{\partial n_F}\right)_T+\tfrac{1}{2}\,\phi_{FF}\phi_{BB}-\phi_{FB}{}^2}{x^2\left(\dfrac{\partial\mu_F{}^0}{\partial n_F}\right)_T+\tfrac{1}{2}\,\phi_{FF}x^2+2\phi_{FB}x(1-x)+\phi_{BB}(1-x)^2},\quad T<T_\lambda(x,p). \tag{3.10}$$

Here $(\partial\mu_F{}^0/\partial n_F)_T$ and $(\partial\mu_B{}^0/\partial n_B)T$ follow from (3.1) and (3.2) and are given by

$$\left(\frac{\partial\mu_F{}^0}{\partial n_F}\right)_T=\frac{\lambda_F{}^3}{-2\beta G_{\frac{1}{2}}(-\exp\beta\mu_F{}^0)}\,,\quad\left(\frac{\partial\mu_B{}^0}{\partial n_B}\right)_T=\frac{\lambda_B{}^3}{\beta G_{\frac{1}{2}}(\exp\beta\mu_B{}^0)}\,. \tag{3.11}$$

We remark that the two expressions (3.9) and (3.10) for $\partial^2 g/\partial x^2$ do *not* become equal at $T=T_\lambda(x,p)$ as the

λ transition in the hard-sphere mixture is in our approximation a second-order phase transition.

For a discussion of the sign of $(\partial^2 g/\partial x^2)_{T,p}$, we remark that the denominators of (3.9) and (3.10) are always positive, so that the behavior of $(\partial\mu_F^0/\partial n_F)_T$ is of crucial importance. Using the fact that $(\partial\mu_F^0/\partial n_F)_T$ is for fixed p an increasing function of T and a decreasing function of x, so that it assumes its minimum at $T=0$, one finds

$$\left(\frac{\partial\mu_F^{\,0}}{\partial n_F}\right)_T \geqslant \left(\frac{\partial\mu_F^{\,0}}{\partial n_F}\right)_{T=0} = \frac{h^2}{4m_F(3\pi^2 xn)^{1/3}} \,. \tag{3.12}$$

With (3.12) one can rule out an instability of the mixture for $T>T_\lambda(x,p)$. For, since $(\partial\mu_B^0/\partial n_B)_T \geqslant 0$, a necessary condition that $(\partial^2 g/\partial x^2)_{T,p}<0$ for $T>T_\lambda(x,p)$ is

$$\frac{\phi_{FB}^{\;2}-\phi_{BB}\phi_{FF}}{2\phi_{FB}} > \left(\frac{\partial\mu_F^{\,0}}{\partial n_F}\right)_T \geqslant \frac{h^2}{4m_F}\,\frac{1}{(3\pi^2 xn)^{1/3}} \quad , \tag{3.13}$$

or with (1.3)

$$xna^3 \geqslant (8\pi/3)\nu^{-3}(1-\nu^{-1})^{-3}\,. \tag{3.14}$$

For a mass ratio $\gamma=\frac{3}{4}$ the right-hand side of (3.14) is of the order of 15 000, so that for $T>T_\lambda(x,p)$ an instability can only occur at densities many times greater than the close packing density. For that reason an instability of the mixture in the region $T>T_\lambda(x,p)$ can be disregarded for the densities in which we are interested.

For $T<T_\lambda(x,p)$, (3.12) leads to the instability condition (2.8) obtained before. Therefore, for $p>p_c$ one finds for the hard-sphere mixture an instability domain in the (x, T) plane, which is bordered on the upper side (i.e., large x) by the λ curve of the mixture [as follows from (3.14)] and on the lower side (i.e., small x) by the solution of the equation

$$\left(\frac{\partial\mu_F^{\,0}}{\partial n_n}\right)_T = \frac{\phi_{FB}^{\;2}-\frac{1}{2}\phi_{FF}\phi_{BB}}{\phi_{BB}} = \frac{ah^2}{4\pi m_F}(\nu+\nu^{-1}) \tag{3.15}$$

as follows from (3.10) and (1.3).

Since $(\partial\mu_F^0/\partial n_F)_T$ increases with T and decreases with x at fixed p, the curve $x_i(T,p)$, representing the solution of (3.15), will with increasing x bend towards the λ curve of the mixture. The point x_s, T_s where the two curves meet is the top of the phase-separation curve (cf. Fig. 2). We have computed the location of the top of the p.s. curve as a function of the reduced pressure from the Eq. (3.15) and the Eq. (3.5a) for the λ curve. In the computation of the top it is convenient to use $\beta\mu_F^0$ as an auxiliary-independent variable. We therefore computed T_s, x_s, $n_s=n(x_s, T_s, p)$ and p from (3.15), (3.5a), (3.1), and (3.8), respectively, as a function of $\beta\mu_F^0$ using the McDougall and Stoner tables of Fermi functions.[17] In Fig. 1 we have plotted (case A) x_s and $T_s^*=T_s/T_\lambda$ as a function of p^*.

IV. THE PHASE-SEPARATION CURVE NEAR $T=0$ AND $T=T_s$

The phase-separation curve and, in particular, the behavior of its two branches $x_l(T,p)$ and $x_u(T,p)$ near $T=0$ and $T=T_s$ follow from the basic equations (1.6).

We have computed (A) the slopes of the p.s. curve at the top and (B) the behavior of the p.s. curve in the immediate neighborhood of $T=0$.

(A) The slopes $dx_l(T_s, p)/dT_s$ and $dx_u(T_s, p)/dT_s$ of the p.s. curve at the top can be found from (1.6), or more conveniently from the equivalent equations (A.1) for g, given in Appendix A, using that $x_u(T,p)$ runs above and $x_l(T,p)$ runs below the λ curve.

The calculations are carried out in Appendix A and are somewhat complicated by the fact that $\partial^2 g(x_s, T_s, p)/\partial x_s^2=0$ when the top is approached along the lower branch of the p.s. curve. The results are as follows:

(1) The slope of the upper branch equals the slope of the λ curve at the top of the p.s. curve and is given by

$$\frac{dx_u(T_s, p)}{dT_s} = \frac{dx_\lambda(T_s, p)}{dT_s}$$

$$= -\frac{3(1-x_s)}{2T_s}\,\frac{x_s+\nu(2-x_s)}{1+\nu}\,S\,, \tag{4.1}$$

where $S=S(x_s, T_s, p)$, defined by

$$S=1-\frac{2}{3}(T_s/n)(\partial n/\partial T_s)_{x_s, p}\,, \tag{4.2}$$

has to be computed with the equation of state (3.8)

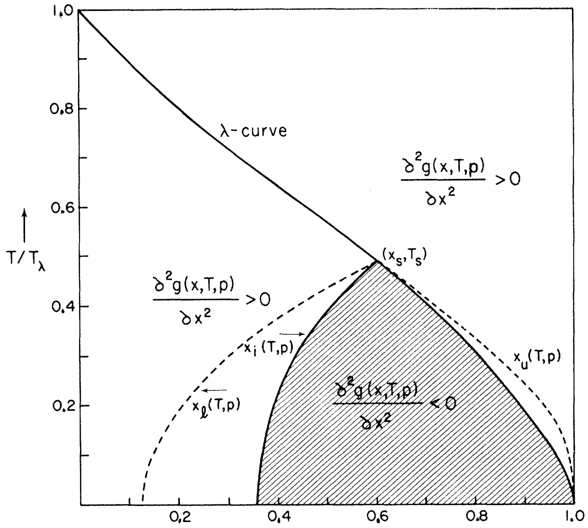

FIG. 2. Instability domain (shaded area) and λ curve in the (x, T) plane. On the upper side the instability domain is bounded by the λ curve, on the lower side by the solution $x_i(T,p)$ of the Eq. (3.15). The lower branch $x_l(T, p)$ and upper branch $x_u(T, p)$ of the p.s. curve run outside the instability domain.

and is found to be of order 1.

The equality (4.1) of the slopes of the upper branch and of the λ curve at the top of the p.s. curve is a direct consequence of the fact that the λ transition in the mixture is a second-order transition in our approximation.[18]

(2) The slope of the lower branch of the p.s. curve at the top is

$$\frac{dx_l(T_s,p)}{dT_s}=\frac{dx_u(T_s,p)}{dT_s}$$

$$\times\left[-\frac{1}{2}+\frac{3x_s}{1-x_s}\left(1-\frac{1}{3S}\,\frac{\mathcal{G}_{\frac{1}{2}}{}^2}{\mathcal{G}_{\frac{3}{2}}\,\mathcal{G}_{-\frac{1}{2}}}\right)\frac{1+\nu}{2\nu}\right]. \tag{4.3}$$

For a wide range of values of $p>p_c$, the ratio of the two slopes is of the order 1.5.

(B) The slopes of the p.s. curve at $T=0$ are infinite, in agreement with the third law of thermodynamics, which holds for this model. The behavior of the p.s. curve near $T=0$ can be found from the Eq. (1.6).

The calculations are carried out in Appendix B and are complicated by the singular behavior of the upper branch $x_u(T,p)$ near $T=0$.

(1) One finds for the upper branch

$$x_u(T,p)\simeq 1-\gamma\, T^{3/2}\exp-\delta/T\ , \tag{4.4}$$

where

$$\gamma=\frac{n(0,T_\lambda,p)}{n(1,0,p)}\;\frac{T_\lambda^{-3/2}}{2.612} \tag{4.5}$$

and

$$\delta=-k^{-1}\,\{\phi_{FB}[x_l n(x_l,0,p)-n(1,0,p)]$$

$$+\phi_{BB}(1-x_l)n(x_l,0,p)\}. \tag{4.6}$$

Here $n(1,0,p)$ and $n(0,\ T_\lambda,p)$ are the density of the mixture at $x=1$ and $T=0$ and at $x=0$ and $T=T_\lambda$, respectively.

(2) Using (4.4), one finds for the behavior of the lower branch $x_l(T,p)$ of the p.s. curve near $T=0$:

$$x_l(T,p)\simeq x_l(0,p)+\alpha T^2, \tag{4.7}$$

where the expression for α is rather involved. α is of the order of $1.5T_\lambda^{-2}$. We remark that the T dependence in (4.7) is due to the fact that both $\mu_F{}^0(x,T,p)$ and $n(x,T,p)$ have such a T dependence. We also remark that the low-temperature behavior (4.7) of $x_l(T,p)$ is determined by the first of the equations (1.6) only.

V. TEMPERATURE-DEPENDENT EXTERNAL PRESSURE $p(T)$

As mentioned already in the introduction, the hard-sphere mixture exhibits a rather large thermal expansion at constant pressure in contrast to helium mixtures. Thus if one chooses, e.g., an external pressure p such that at $T=0$ and $x=0$ the hard-sphere mixture has a density of the order of that of a helium mixture at $T=0$ and $x=0$, the density of the hard-sphere mixture would have decreased by about 40% at $T=T_\lambda$ at the same p and x, while the density of a helium mixture under similar conditions changes only by about 1%.

The decrease in density can be compensated by a corresponding increase in external pressure. Within the model, there is no unique way of choosing such a compensating pressure p. In order to investigate the effect of an adjusted pressure on the phase separation of the mixture, we consider in this section the case that the external pressure p only depends on the temperature, i.e., $p=p(T)$ and the function $p(T)$ is chosen in such a way that the density of the pure Bose component remains the same for all T.[19]
As we shall see below, with this choice one can use all the formulas of the preceding section with the only modification that p is replaced by $p(T)$.

The function $p(T)$ follows from the condition:

$$n(0,T,p(T))=n(0,0,p(0)). \tag{5.1}$$

This condition clearly leaves $p(0)$, or equivalently $n[0,0,p(0)]$, still a free parameter. $p(T)$ can be solved from (5.1) by using the equation of state (3.8), which gives p as functions of x, T, and n. Thus

$$p(T)\equiv p[0,T,n(0,T,p(T))]$$

$$=p[0,T,n(0,0,p(0))] \tag{5.2}$$

which, with (3.8) and (3.5b), leads to the equation

$$p(T)=kT\lambda_B^{-3}1.342+\tfrac{1}{2}\phi_{BB}\,[n^2(0,0,p(0))$$
$$+(2.612)^2\lambda_B^{-6},],\quad T<T_\lambda \tag{5.3}$$

for $p(T)$. As the pressure p enters into the formulas of the phase separation only through the density $n(x,T,p)$ it suffices to determine now $n(x,T,p(T))$, which is determined by the equation

$$p(T)=-2kT\lambda_F^{-3}\mathcal{G}_{\frac{5}{2}}(-\exp\beta\mu_F^{0})$$
$$+kT\lambda_B^{-3}\,\mathcal{G}_{\frac{5}{2}}(\exp\beta\mu_B^{0})$$
$$+\{\tfrac{1}{4}\phi_{FF}x^2+\phi_{FB}x(1-x)+\tfrac{1}{2}\phi_{BB}(1-x)^2$$
$$\times[1+(1-\xi)^2]\}n^2(x,T,p(T)), \tag{5.4}$$

where $p(T)$ is given by (5.3) and where the Eqs. (3.1) and (3.2) [or (3.5b)] relate μ_F^0 and μ_B^0 (or ξ) to $n(x,T,p(T))$.

Thus, all the formulas of the previous sections remain valid for this case (case B), if one replaces everywhere p by $p(T)$ of (5.3). We remark that when we now consider $n(x,T,p(T))$ as a function of x, T and the free parameter $p(0)$, we obtain of course a function which is different from the function $n=n(x,T,p)$ considered in the previous section.

As a consequence of the above, all results obtained in the previous sections remain qualitatively the same while those at $T=0$ are not affected at all.

In Fig. 1 we have drawn the curves for x_S and T_S/T_λ as a function of $p^*=p^*(0)$ (case B). In Fig. 3 we have drawn the p.s. curve (solid line) as calculated on the basis of (5.2) and (5.3) for $p^*=0.13$ and $\nu=\frac{3}{4}$. The value $p^*=0.13$ corresponds to a value $n(0,0,p(0))a^3=0.365$, which is the reduced density of He^4 at $T=0$, when one takes for the hard-sphere diameter a, the value 2.556 Å, which equals the value of σ of the 12-6 Lennard-Jones potential for helium, as determined by de Boer and Michels.

Characteristics of this hard-sphere p.s. curve are

$$x_l(0)=0.125,\quad \frac{dx_l(T_s,p(T_s))}{dT_s}=2.07T_\lambda^{-1};$$
$$x_s(0)=0.602,\quad \frac{dx_u(T_s,p(T_s))}{dT_s}=1.28T_\lambda^{-1}; \tag{5.5}$$
$$\frac{T_s}{T_\lambda}=0.492,\quad \frac{dx_\lambda(T_s,p(T_s))}{dT_s}=1.28T_\lambda^{-1};$$
$$\alpha=1.50T_\lambda^{-2},\quad \gamma=0.429T_\lambda^{-3/2},\quad \delta=0.120T_\lambda$$

For comparison we have also drawn the p.s. curve for He mixtures (dashed line) in the same figure.

Characteristics of the helium p.s. curve are[20]

$$x_l(0)=0.064,\quad \frac{dx_l(T_s,p_s)}{dT_s}=5.38T_\lambda^{-1};$$
$$x_s(0)=0.669,\quad \frac{dx_u(T_s,p_s)}{dT_s}=1.54T_\lambda^{-1}; \tag{5.6}$$
$$\frac{T_s}{T_\lambda}=0.405,\quad \frac{dx_\lambda(T_s,p_s)}{dT_s}=0.84T_\lambda^{-1};$$
$$\alpha=3.24T_\lambda^{-2},\quad \gamma=3.45T_\lambda^{-3/2},\quad \delta=0.327T_\lambda.$$

We remark that the choice $a=2.556$ Å has no theoretical basis and was only made to obtain a value of p^* of the correct order of magnitude. Changes of about 10% in a lead to values of $x_l(0)$, x_S, and T_S/T_λ identical with those found in He mixtures. It should be remarked, however, that these 10% changes in a are not consistent, as a has to be increased to give the helium value of $x_l(0)$, but decreased to obtain the helium values of x_S and T_S/T_λ.

VI. DISCUSSION

With respect to the results obtained in the previous sections, we would like to make the following remarks:

(1) The phase separation is not a true low-density property of the hard-sphere mixture (i.e., it does *not* persist in the limit $na^3\to 0$). but only appears at (reduced) densities of the order of $\pi/24$. Whether it is a true property of a dense hard-sphere mixture can only be decided by taking into account terms of higher order in the interaction a than have been considered in this paper. That phase separation might well be a property of a dense hard-sphere mixture is perhaps indicated by a preliminary investigation carried out at $T=0$, which showed that the inclusion of higher-order interaction terms in the calculation encourages phase separation in the mixture.[7]

(2) In the approximation used here, the excitation spectrum of the condensed Bose component exhibits a gap, while it has been shown that a condensed Bose system of hard spheres has phonon-like excitations instead.[3,15] We have therefore investigated what the effect on the phase separation of the mixture would be if an excitation spectrum for the Bose component is considered, which takes due account of the phononlike character of its low-lying excitations. In particular, we have studied the properties of the mixture on the basis of the following expression for the free energy[15]:

$$F(N_F,N_B,V,T)=F_F^0(N_F,V,T)$$
$$+kT\sum_{k\neq 0}\ln(1-\exp-\beta\hbar\omega_k)$$

$$+(1/2V)\{\tfrac{1}{2}\phi_{FF}N_F{}^2+2\phi_{FB}N_FN_B$$

$$+\phi_{BB}N_B{}^2\,[1+(1-\xi)^2]\}. \qquad (6.1)$$

Here $F_F{}^0$ is again given by (3.6b), while $\hbar\omega_k$ the phononenergy is given by

$$\hbar\omega_k=(\hbar^2/2m_B)k\,[k^2+16\pi an(1-x)\xi]^{1/2}\ . \qquad (6.2)$$

The value of ξ, the fraction of the Bose particles with zero momentum, is given by

$$(1-x)(1-\xi)=\frac{1}{V}\sum_{k\neq 0}\frac{k}{[k^2+16\pi an(1-x)\xi]^{1/2}}$$

$$\times\exp(-\beta\hbar\omega_k)/(1-\exp-\beta\hbar\omega_k). \qquad (6.3)$$

We note that for $T=0$, when no phonons are present, (6.1) reduces to (2.1). The main difference between (6.1) and (3.6a) is that the pure Bose contribution to F in (6.1) behaves for small T as T^4, whereas it behaves as $T^{3/2}$ [because of the $(2-\xi^2)$ term] in (3.6a).[21]

Computation of the low-temperature properties of the mixture [i.e., for $T \ll T_\lambda(x,p)$] on the basis of (6.1) instead of (3.6a) does not reveal any significant change either qualitatively or quantitatively in the phase-separation curve. In particular, the low-temperature behavior of the p.s. curve, as given by the Eqs. (4.4) and (4.7), is not changed and the constants α, γ, δ are not affected by the replacement of (3.6a) by (6.1).

(3) The dependence of the p.s. curve on the external pressure – or equivalently on the density of the mixture – leads to the prediction that $x_l(0)$ decreases, while T_S/T_λ increases slightly with increasing pressure in the hard-sphere mixture.

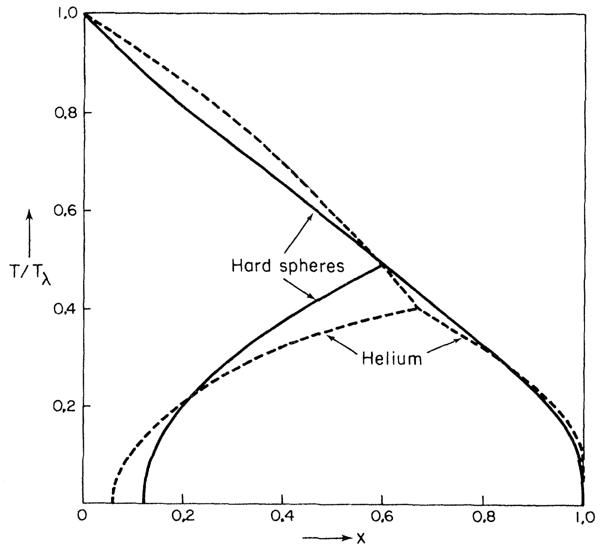

FIG. 3. Reduced phase diagram for hard sphere [solid line, case (B), $\nu=\frac{3}{4}$, $p^*(0)=0.13$)] and for He mixtures (dashed line).

(4) Figure 3 and the Equations (5.2) and (5.3) indicate that the phase separation found in the hard-sphere mixture is qualitatively similar and quantitatively close to that found in He mixtures. An exception seems to be the continuity of the slopes of the λ curve and the upper branch of the p.s. curve found in the hard-sphere mixture which does not seem to be present in He mixtures.[6] As this continuity of slopes is a direct consequence of the fact that the λ transition is a second-order transition in the hard-sphere mixture, this would indicate that the λ transition is not a second-order transition in He mixtures, at least at the top of the p.s. curve.

(5) In order to obtain a better quantitative agreement with He mixtures, it is necessary to include the effect of the attractive force in the model calculations, in some way other than by a temperature-dependent external pressure, which keeps the hard-sphere mixture together. Preliminary calculations based on a model in which an over-all negative potential is added to the free energy such as to give the mixture a zero pressure, have been carried out by T.T. Wu and one of the authors (E.G.D.C.) and lead to encouraging results.

(6) We would like to mention in conclusion that the chemical potentials of the Bose component $\mu_B(x,T,p)$ as computed in this paper also yield the osmotic pressure Π of a mixture of concentration x in equilibrium with the pure Bose components according to the relation

$$\mu_B(x,T,p)=\mu_B(0,T,p-\Pi)\ . \qquad (6.4)$$

Using (3.7) and (5.4) one can develop Π in a power series in the concentration x for low concentrations[22]:

$$\Pi=xnkT\,[1+q_1(T,p)x+q_2(T,p)x^2], \qquad (6.5)$$

where for $\nu=\frac{3}{4}$, q_1 and q_2 are given by (case B)

$$q_1=\frac{n\lambda_F{}^3}{2^{7/2}}-\left(\frac{1}{6}+\frac{25}{36}b+\frac{1}{2b}\right),$$

$$q_2=-\left(\frac{1}{3}+\frac{1}{2b}\right)q_1+\frac{2}{3}-\frac{1}{12b}-\frac{1}{8b^2}-\frac{1}{b}\frac{n\lambda_F{}^3}{2^{7/2}} \qquad (6.6)$$

$$+\frac{1}{8}\left(\frac{1}{4}-\frac{1}{3^{3/2}}\right)(n\lambda_F{}^3)^2$$

with $n=n(0,\mathrm{T},p(T))$ and $b=an\lambda_B{}^2$.

In Fig. 4 we have drawn curves for q_1 and q_2 as a function of $T^*=T/T_\lambda$ for $p^*=0.13$, together with the curve for q_1 based on the theory of Bardeen, Baym, and Pines and some experimental points derived from the data of Wilson, Edwards,

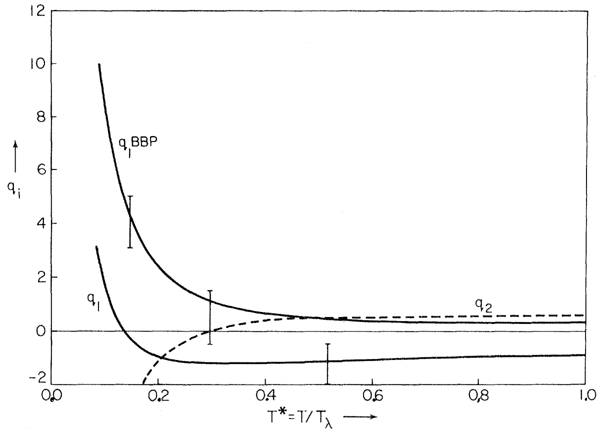

FIG. 4. Expansion coefficients q_1 and q_2 (dashed line) of the osmotic pressure in powers of the fermion concentration x as a function of $T^* = T/T_\lambda$ for hard-sphere mixtures. For comparison, q_1, derived from the theory of Bardeen, Baym, and Pines (Refs. 8 and 23) (q_1^{BBP}), as well as from measurements of Wilson, Edwards, and Tough (Ref. 23) are also given. The error bars indicate the estimated uncertainty of the measurements.

and Tough[23] (the large error bars indicate the difficulty to obtain a value for q_1 from the reported data).

Note added in proof: The curve q_1^{BBP} in Fig. 4 is drawn incorrectly and runs appreciably lower, passing a. o. through the points 0 for $T = 0.23T_\lambda$ and − 0.25 for $T = 0.5T_\lambda$.

ACKNOWLEDGMENT

The authors wish to express their gratitude to B. M. Mossel for his collaboration in the calculation of the properties of the hard-sphere mixture at constant density.[24]

APPENDIX A. CALCULATION OF THE SLOPES AT THE TOP OF THE PHASE-SEPARATION CURVE

In this appendix we shall derive the Eqs. (4.1), (4.2), and (4.3) for the slopes of the upper branch $x_u(T,p)$ and the lower branch $x_l(T,p)$ at the top x_s, T_s of the p.s. curve. The argument p will be dropped in this appendix.

It proves convenient to base the computation, instead of on Eq. (1.6), on the equivalent set

$$g_x^{+}(x_u(T),T) = g_x^{-}(x_l(T),T),$$
$$g^{+}(x_u(T),T) - x_u(T) g_x^{+}(x_u(T),T) = g^{-}(x_l(T),T) - x_l(T) g_x^{-}(x_l(T),T). \tag{A. 1}$$

Here the subscript x means differentiation with respect to x, so that $g_x = (\partial g/\partial x)_T$. The superscripts + and − refer to the expression for g above and below the λ curve. This distinction is necessary as $x_u(T)$ runs above the λ curve and $x_l(T)$ runs below the λ curve. Expanding both sides of the Eqs. (A. 1) around the top (x_s, T_s) and introducing for convenience the following additional abbreviations

$$x_u(T) - x_s = \Delta x_u, x_l(T) - x_s = \Delta x_l, \quad T - T_s = \Delta T,$$
$$g_x^{+}(x_s,T_s) = g_x^{+}, \quad g_{xx}^{+}(x_s,T_s) = g_{xx}^{+}, \text{ etc.}; \quad g_{xx}^{+} - g_{xx}^{-} = \Delta g_{xx}, \text{ etc.}, \tag{A. 2}$$

we obtain the equations:

$$0 = \Delta g_x + g_{xx}^{+}\Delta x_u - g_{xx}^{-}\Delta x_l + \Delta g_{xT}\Delta T + (1/2!)\{[g_{xxx}^{+}(\Delta x_u)^2 - g_{xxx}^{-}(\Delta x_l)^2]$$
$$+ 2(g_{xxT}^{+}\Delta x_u - g_{xxT}^{-}\Delta x_l)\Delta T + \Delta g_{xTT}(\Delta T)^2\} + \cdots \tag{A. 3}$$

and

$$0 = \Delta g_T \Delta T + (1/2!)[\Delta g_{TT}(\Delta T)^2 - g_{xx}^{+}(\Delta x_u)^2 - g_{xx}^{-}(\Delta x_l)^2]$$
$$+ (1/3!)\{\Delta g_{TTT}(\Delta T)^3 - 3[g_{xTT}^{+}(\Delta x_u)^2 - g_{xTT}^{-}(\Delta x_l)^2]\Delta T - 2[g_{xxx}^{+}(\Delta x_u)^3 - g_{xxx}^{-}(\Delta x_l)^3]\} + \cdots . \tag{A. 4}$$

Since the λ transition in the mixture is a second-order transition we have the following relations:

$$\Delta g_x = \Delta g_T = 0, \tag{A.5a}$$

$$\dot{x}_\lambda = dx_\lambda(T)/dT = -\Delta g_{xT}/\Delta g_{xx} = -\Delta g_{TT}/\Delta g_{xT}, \tag{A.5b}$$

$$\Delta g_{xxx}\dot{x}_\lambda{}^3+3\Delta g_{xTT}\dot{x}_\lambda{}^2+3\Delta g_{xTT}\dot{x}_\lambda+\Delta g_{TTT}=0, \tag{A.5c}$$

where $\dot{x}_\lambda=dx_\lambda/dT$ is the slope of the λ curve.

In order to derive the slopes of the two branches of the phase separation curve, we consider first the leading terms in (A. 3) and (A. 4), using (A. 5a) and $g_{xx}{}^-=0$ (so that $\Delta g_{xx}=g_{xx}{}^+$):

$$\Delta g_{xx}\Delta x_u+\Delta g_{xT}\Delta T=0, \quad \Delta g_{xx}(\Delta x_u)^2-\Delta g_{TT}(\Delta T)^2=0. \tag{A. 6}$$

In view of (A. 5b), these two equations have the same solution for Δx_u:

$$\Delta x_u/\Delta T=-\Delta g_{xT}/\Delta g_{xx}=\dot{x}_\lambda(T_s) \tag{A. 7}$$

so that

$$\frac{dx_u(T_s)}{dT_s}=\lim_{\Delta T\to 0}\frac{\Delta x_u}{\Delta T}=-\frac{\Delta g_{xT}}{\Delta g_{xx}}=\dot{x}_\lambda(T_s). \tag{A. 8}$$

Thus the slopes of the *upper* branch of the p.s. curve and that of the λ curve are equal at the top of the p.s. curve [first equality of Eq. (4. 1)].

In order to find the slope of the *lower* branch at the top of the p.s. curve, we eliminate the leading terms of (A. 3) and (A. 4), by multiplying (A. 3) by $\frac{1}{2}(\Delta x_u+\dot{x}_\lambda\Delta T)$ and adding the result to (A. 4), and find

$$\begin{aligned}&[g_{xxx}{}^-(2\Delta x_l+\Delta x_u)+3g_{xxT}{}^-\Delta T](\Delta x_u-\Delta x_l)(\Delta x_l-\dot{x}_\lambda\Delta T)\\ &\quad=-\tfrac{1}{2}g_{xxx}{}^-(\Delta x_u-\Delta x_l)^2(\Delta x_u-\dot{x}_\lambda\Delta T)+\Delta g_{xxx}(\Delta x_u)^2(-\tfrac{1}{2}\Delta x_u+\tfrac{3}{2}\dot{x}_\lambda\Delta T)\\ &\quad\quad+3\Delta g_{xxT}\Delta x_u\dot{x}_\lambda(\Delta T)^2+\tfrac{3}{2}\Delta g_{xTT}(\Delta x_u+\dot{x}_\lambda\Delta T)(\Delta T)^2+\Delta g_{TTT}(\Delta T)^3.\end{aligned} \tag{A. 9}$$

Inserting the first-order solution (A. 7) into (A. 9) and using (A. 5c), one finds that the right-hand side of (A. 9) vanishes. Since $\Delta x_l\neq\Delta x_u\simeq\dot{x}_\lambda\Delta T$ we find

$$\Delta x_l/\Delta T=-\tfrac{1}{2}\Delta x_u/\Delta T-\tfrac{3}{2}g_{xxT}{}^-/g_{xxx}{}^- \tag{A. 10}$$

so that

$$\frac{dx_l(T_s)}{dT_s}=\lim_{\Delta T\to 0}\frac{\Delta x_l}{\Delta T}=-\frac{1}{2}\frac{dx_u(T_s)}{dT_s}-\frac{3g_{xxT}{}^-}{2g_{xxx}{}^-}. \tag{A. 11}$$

We now derive from (A. 8) and (A. 11) the expressions for $dx_u(T_s)/dT_s$ and $dx_l(T_s)/dT_s$ given in Sec. 4.

The slope of the λ curve can be computed from (3. 5a), and the result is

$$\frac{dx_\lambda(T)}{dT}=-\frac{3(1-x_\lambda)}{2T_\lambda}\left[1-\frac{2T}{3n}\left(\frac{\partial n}{\partial T}\right)_{x,p}\right]\left[1-\frac{1-x_\lambda}{n}\left(\frac{\partial n}{\partial x}\right)_{T,p}\right]^{-1}. \tag{A. 12}$$

From (3. 10) one obtains by differentiation with respect to x and T

$$g_{xxT}{}^-/g_{xxx}{}^-=\frac{\partial}{\partial T_s}\left(\frac{\partial\mu_F{}^0}{\partial n_F}\right)_{T_s}\ \frac{\partial}{\partial x_s}\left(\frac{\partial\mu_F{}^0}{\partial n_F}\right)_{T_s}, \tag{A. 13}$$

where with (3. 11) and (3. 1) it is found that

$$\frac{\partial}{\partial T_s}\left(\frac{\partial\mu_F{}^0}{\partial n_F}\right)_{T_s}=\frac{\lambda_{F,s}{}^3}{2\beta_s\mathcal{G}_{\frac{1}{2}}}\frac{1}{2T_s}\left\{1+\frac{3\mathcal{G}_{\frac{3}{2}}\mathcal{G}_{-\frac{1}{2}}}{\mathcal{G}_{\frac{1}{2}}{}^2}\left[1-\frac{2T_s}{3n}\left(\frac{\partial n}{\partial T_s}\right)_{x_s,p}\right]\right\} \tag{A. 14}$$

and

$$\frac{\partial}{\partial x_s}\left(\frac{\partial \mu_F{}^0}{\partial n_F}\right)_{T_s} = \frac{\lambda_{F,s}{}^3}{2\beta_s \mathcal{G}_{\frac{1}{2}}} \frac{\mathcal{G}_{\frac{3}{2}} \mathcal{G}_{-\frac{1}{2}}}{\mathcal{G}_{\frac{1}{2}}{}^2}\left[\frac{1}{x_s} + \frac{1}{n}\left(\frac{\partial n}{\partial x_s}\right)_{T_s, p}\right]. \tag{A. 15}$$

The formulas (A. 12) and (A. 15) simplify at the top of the p. s. curve, as it follows from (3. 8) and (3. 15) that

$$\frac{1}{n}\left(\frac{\partial n}{\partial x_s}\right)_{T_s, p} = \frac{\phi_{BB} - \phi_{FB}}{x_s \phi_{FB} + (1-x_s)\phi_{BB}}. \tag{A. 16}$$

Inserting (A. 16) in (A. 12) for $T = T_s$ yields the second equality of (4. 1). Inserting (A. 16) in (A. 15) and (A. 15) and (A. 14) in (A. 11) yields Eq. (4. 3).

APPENDIX B. THE BEHAVIOR OF THE PHASE SEPARATION CURVE NEAR $T = 0$

In this appendix we derive the expressions (4. 4)–(4. 7) for the behavior of the phase-separation curve near $T = 0$. The calculation is based on the coexistence Eqs. (1. 6), which read explicitly with (3. 7) (suppressing the argument p)

$$\begin{aligned} &\mu_F{}^0(x_u(T), T) + \{\tfrac{1}{2}\phi_{FF} x_u(T) + [1 - x_u(T)]\phi_{FB}\} n(x_u(T), T) \\ &\qquad = \mu_F{}^0(x_l(T), T) + \{\tfrac{1}{2}\phi_{FF} x_l(T) + [1 - x_l(T)]\phi_{FB}\} n(x_l(T), T) \end{aligned} \tag{B. 1a}$$

and

$$\begin{aligned} &\mu_B{}^0(x_u(T), T) + \{\phi_{FB} x_u(T) + 2\phi_{BB}[1 - x_u(T)]\} n(x_u(T), T) \\ &\qquad = \{\phi_{FB} x_l(T) + \phi_{BB}[1 - x_l(T)][2 - \xi(x_l(T), T)]\} n(x_l(T), T). \end{aligned} \tag{B. 1b}$$

We found already in Sec. 2 that $x_u(0) = 1$. The behavior of the upper branch of the p.s. curve near $T = 0$ is complicated by the peculiar behavior of $\mu_B{}^0(x_u(T), T)$ near $x_u(0) = 1$ and $T = 0$, which makes $n_B \lambda_B{}^3 = [1 - x_u(T)] n(x_u(T), T)\lambda_B{}^3$ exponentially small for $T \to 0$. For $n_B \lambda_B{}^3$ and $\mu_B{}^0$ are related by (3.2)

$$n_B \lambda_B{}^3 = \mathcal{G}_{\frac{3}{2}}(\exp \beta \mu_B{}^0). \tag{B. 2}$$

Inverting this expression, one finds $\mu_B{}^0$ as the following series in terms of $n_B \lambda_B{}^3$:

$$\mu_B{}^0 = kT\left\{\ln n_B \lambda_B{}^3 - n_B \lambda_B{}^3 + \left(\frac{1}{4} - \frac{1}{3^{3/2}} - \frac{1}{2^{5/2}}\right)(n_B \lambda_B{}^3)^2 + \cdots\right\}. \tag{B. 3}$$

The series (B. 3) converges for $T \geq T_\lambda(x)$. Thus $\mu_B{}^0$ will tend to zero for $T \to 0$, unless $n_B \lambda_B{}^3$ becomes exponentially small, such that $kT \ln n_B \lambda_B{}^3$ stays finite. This indeed has to occur along the upper branch, since for $T \to 0$, the Eq. (B.1b) yields for $\mu_B{}^0$ the *finite* result [using $\xi(x_l(0), 0) = 1$]:

$$\lim_{T \to 0} \mu_B{}^0(x_u(T), T) = \{\phi_{FB} x_l(0) + \phi_{BB}[1 - x_l(0)]\} n(x_l(0), 0) - \phi_{FB} n(1, 0) = -\delta k. \tag{B. 4}$$

The parameter δ depends on $x_l(0)$ and is found to be positive for the $x_l(0)$ obtained Sec. 2.

Therefore the finite limit of $\mu_B{}^0(x_u(T), T)$ for $T \to 0$ implies that $n_B \lambda_B{}^3$ decreases exponentially to zero when $T \to 0$. This in turn determines the behavior of the upper branch $x_u(T)$ for $T \to 0$ because with (B. 4) and (B. 3) we have

$$-\delta k = \lim_{T \to 0} \mu_B{}^0(x_u(T), T) = \lim_{T \to 0} kT \ln n_B \lambda_B{}^3 = \lim_{T \to 0} kT \ln [1 - x_u(T)]\lambda_B{}^3 n(x_u(T), T) \tag{B. 5}$$

so that $x_u(T)$ behaves for $T \to 0$

$$x_u(T) = 1 - \gamma T^{3/2} \exp -\delta/T \tag{B. 6}$$

with δ given by (B. 4) and γ given by

$$\gamma = \frac{1}{n(1, 0)} \frac{1}{\lambda_B{}^3 T^{3/2}} = \frac{1}{2.612} \frac{n(0, T_\lambda)}{n(1, 0)} T_\lambda{}^{-3/2}. \tag{B. 7}$$

We remark that the behavior of $x_u(T)$ near $T=0$ as given by (B. 6) is determined only by Eq. (B. 1b) and the value $x_l(0)$ obtained in Sec. 2.

The behavior of $x_l(T)$ near $T=0$ can be found from Eq. (B. 1a) by inserting (B. 7) for $x_u(T)$ and neglecting exponentially small terms:

$$\mu_F{}^0(x_l(T),T)+\{\tfrac{1}{2}\phi_{FF}x_l(T)+\phi_{FB}[1-x_l(T)]\}n(x_l(T),T)=\mu_F{}^0(1,T)+\tfrac{1}{2}\phi_{FF}n(1,T). \tag{B. 8}$$

For $T=0$, (B. 8) leads to the value $x_l(0)$ already determined in Sec. 2. All functions occurring in (B. 8) are regular around $x=x_l(0)$ and $T=0$. Expanding the various functions in powers of $x_l(T)-x_l(0)$ and T, the leading terms are of order T^2. Thus, $x_l(T)$ behaves for $T\to 0$ as

$$x_l(T)=x_l(0)+\alpha T^2, \tag{B. 9}$$

where $\alpha T_\lambda{}^2$ can be expressed for a given ν in terms of $x_l(0)$, $n(0,T_\lambda)$, $n(x_l(0),0)$, and $n(1,0)$.

For $\gamma=\frac{3}{4}$ one finds with $x_l(0)=0.125$, $\alpha=3.24T_\lambda{}^{-2}$, the value quoted in the main text.

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[10] A different model, which also leads to the usual coexistence conditions, has been investigated at the same time by T. T. Wu and one of us (E.G.D.C.) (see also Sec. 6, Sub. 5).

[11] The second equation (1.6) will be used in Sec. 4, where the behavior of $x_u(T,p)$ in the immediate neighborhood of $T=0$ will be discussed.

[12] p_{max} follows from the equation $\mu_F(0,0,p_{\text{max}}) = \mu_F(1,0,p_{\text{max}})$. It turns out that in our approximation p_{max} is large and corresponds to a reduced density na^3 of approximately 0.8, which is far outside the domain of validity of the approximation.

[13] We note that in a similar treatment a Fermi-Fermi mixture (equal spins) would at $T=0$ exhibit an incomplete phase separation starting near $x=1/2$, whereas a Bose-Bose mixture would exhibit a complete phase separation at $T=0$.

[14] We note, however, that the nature of the λ transition is affected by the hard-sphere interaction, as it is a second-order transition instead of a first-order transition, which is the case for an ideal gas mixture [cf. Eqs. (3.9) and (3.10)].

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[16] The expression (3.6) for the free energy is based on an energy spectrum of the Bose component, that contains an unrealistic gap and should not be used at very low temperatures, when $a\lambda_B{}^2 n_B \gg 1$. However, the results obtained on the basis of (3.6) in this and the following section do not depend on these features, as will be discussed in Sec. 6, Sub. 2.

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[19] We remark that this resembles the situation of helium mixtures where measurements are usually not carried out at constant external pressure but at the vapor pressure $p=p_S(x,T)$, which varies both with x and T. It would seem therefore most appropriate for a comparison with the behavior of helium mixtures to consider an external pressure p which varies both with x and T such that the density of the hard-sphere mixture varies with x and T as that of helium mixtures under the vapor pressure. For simplicity, however, we consider in this section, only the case in which the external pressure of the hard-sphere mixture varies with T and not with x.

[20] The large difference in γ in (5.5) and (5.6) is perhaps not as significant as it might seem. For, the He values of γ and δ in (5.6) were taken from D. O. Edwards and J. G. Daunt [Phys. Rev. 124, 640 (1961)], who derived the low-temperature behavior (4.4) of the upper branch of the helium phase-separation curve, using an effective mass $m_B{}^* = 5.4m_B$ to fit the experimental data. It should be noted, however, that this fit is very sensitive to the value of δ and that the experimental data do not seem to extend to sufficiently low temperatures, in order to permit an unambiguous determination of δ and γ.

[21] The term proportional to $T^{3/2}$ in (3.6) has no influence on the phase separation, however, as it is linear in x and independent of V.

[22] The authors are indebted to V. J. Emery for calling their attention to the fact that for the series expansion (6.5) of Π in powers of x, one has to include in the expansion of (6.4) for small Π, also higher powers in Π than the first.

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