

## Ground state of isotopic fermion-boson mixtures

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An investigation of the ground-state configuration of isotopic fermion-boson mixtures is reported for both two and three dimensions. A detailed numerical study of systems interacting with Lennard-Jones-type potentials is presented, enabling one to interpret these results in terms of a picture of the fermion-boson mixture as being built up from an "underlying" boson-boson mixture. It is thus possible to argue that the presence of Fermi-Dirac statistics in one of the constituents is a necessary condition for miscibility in the ground state of an isotopic mixture. Further a criterion is presented for the fermion chemical potentials which is used to distinguish those mixture systems whose ground state is complete separation from those systems whose ground state is at least partially mixed. Finally the analysis is applied to the helium and spin-polarized hydrogen isotopic mixtures (in two and three dimensions) and, wherever possible, the calculated numbers are compared to experiment.

### I. INTRODUCTION

Since the first report of phase separation in  $^3\text{He}$ - $^4\text{He}$  mixtures by Walters and Fairbank<sup>1</sup> in 1956, the isotopic quantum liquid mixtures have undergone intensive experimental and theoretical scrutiny. A milestone in the understanding of these systems came with the suggestion by Edwards and Daunt<sup>2</sup> in 1961 that the phase separation was incomplete at low  $^3\text{He}$  concentrations. Cohen and van Leeuwen<sup>3,4</sup> investigating a mixture of isotopic hard-sphere fermions and bosons also found indications of the possibility of an incomplete phase separation at  $T=0$  K. In 1965 the existence of a partially mixed ground state was confirmed by Edwards, Brewer, Seligmann, Skertic, and Yaqub.<sup>5</sup> However, most of the theoretical attention to the mixture system (at low temperatures) has not been addressed to the phenomenon of incomplete separation per se but rather to the *consequences* of this phenomenon: i.e., the existence of a Fermi liquid whose density and temperature can be easily varied.<sup>6</sup> Indeed, other than the molecular dynamics of Hansen and Schiff,<sup>7</sup> calculations of the properties of  $^3\text{He}$ - $^4\text{He}$  mixtures<sup>8-10</sup> have been concerned with the difficult task of obtaining the  $^3\text{He}$  effective mass, the  $^3\text{He}$ - $^3\text{He}$  effective interaction, etc.

In this paper we address the question of the ground-state configuration of  $^3\text{He}$ - $^4\text{He}$  mixtures and the general question of phase separation in boson-fermion mixtures. We have been motivated into reexamining this problem by several developments.

(i) There is at present a large experimental effort<sup>11</sup> to examine the possibility of producing (meta-)stable samples of atomic hydrogen interacting in the  $b^3\Sigma_u^+$

state.<sup>12</sup> Hydrogen has, of course, three isotopes of which  $^1\text{H}$  and  $^3\text{H}$  (half-life 12.3 yr) are expected to be composite bosons and  $^2\text{H}$  a composite fermion. Thus we might ask about the ground state of deuterium-hydrogen and deuterium-tritium mixtures. (The hydrogen-tritium or boson-boson mixture has been treated previously.<sup>13</sup>)

(ii) In recent years the  $^3\text{He}$ - $^4\text{He}$  system has been studied in various geometries from thick films to physisorbed submonolayers. These systems are difficult to study formally because of their intrinsic inhomogeneity (i.e., the presence of defining walls). Thus one would like to have available a basic understanding of the *bulk* mixture ground state to serve as a guide for choosing those elements necessary for a model description of the inhomogeneous ground state.

In this paper we have investigated the ground-state configuration of a large class of binary fermion-boson mixtures using standard computational tools: Slater-Jastrow wave functions, hypernetted chain (HNC)  $g(r)$ 's, etc. We show that the question of whether or not there is mixing of fermions in bosons can be answered by examining the "underlying" isotopic boson-boson mixture. An important feature of our picture of the mixing process is that one may draw conclusions concerning the mixture using one's knowledge of the chemical potentials of the *pure* phases. We support this picture with the results of detailed numerical calculations of the ground state of two- and three-dimensional mixtures.

The plan of the paper is the following. In Sec. II we outline the Slater-Jastrow approach to calculations of the properties of fermion-boson mixtures and derive those formulas we have employed in calculat-

ing the energy, enthalpy, chemical potentials, etc., as functions of pressure and concentration. In Sec. III we discuss a general class of fermion-boson mixtures using a scaled set of units with appropriate fermion and boson de Boer parameters. We introduce a picture of the mixing energetics that builds up the fermion system from the boson system and provides a definite answer to the old question concerning whether it is mass or statistics which drives the phase mixing. This picture also permits us to establish a simple criterion for determining whether or not a mixture has finite solubility, completely phase separates, etc. This criterion is verified by detailed calculation of the properties of mixtures. We specialize, in Sec. IV, to the  $^3\text{He}$ - $^4\text{He}$  system and describe the results of calculations of many mixture properties: the maximum solubility as a function of pressure, the Bardeen Baym, and Pines (BBP)<sup>14</sup> parameter  $\alpha$ , the  $^3\text{He}$  zero-concentration chemical potential as a function of pressure, the position of the spinodal line as a function of pressure, and the osmotic pressure. Section V contains a brief review of our results and some remarks about the limitations of the analysis we have presented.

## II. THEORY

In this section we derive the formal expression for the energy, enthalpy, chemical potentials, etc., of the mixture systems that are employed in our numerical studies.

We consider a homogeneous, isotopic mixture of the  $N_B$  bosons and  $N_F$  fermions (with  $\nu$  equally populated Fermi seas) confined to a  $d$ -dimensional box of volume  $V$  where  $N = N_B + N_F$  and  $d = 2, 3$ . The Hamiltonian for the system is

$$H = -\frac{\hbar^2}{2m_B} \sum_{i=1}^{N_B} \nabla_i^2 - \frac{\hbar^2}{2m_F} \sum_{i=1}^{N_F} \nabla_i^2 + \sum_{1 \leq i < j \leq N_B} V_{BB}(r_{ij}) + \sum_{\substack{i=1, N_B; \\ j=1, N_F}} V_{BF}(r_{ij}) + \sum_{1 \leq i < j \leq N_F} V_{FF}(r_{ij}), \quad (2.1)$$

where  $V_{\alpha\beta}$  is the potential function. (Here and henceforth we use greek subscripts  $\alpha$  and  $\beta$  to stand for  $B$  or  $F$ .) In this paper we shall consider systems of particles interacting with a Lennard-Jones-type 6-12 potential

$$V_{\alpha\beta} = 4\epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^6 \right], \quad (2.2)$$

where, for isotopic mixtures,  $\epsilon_{BB} = \epsilon_{BF} = \epsilon_{FF} \equiv \epsilon$  and  $\sigma_{BB} = \sigma_{BF} = \sigma_{FF} \equiv \sigma$ . In Sec. IV where we consider helium we use the de Boer-Michels values

$$\epsilon = 10.22 \text{ K}, \quad \sigma = 2.556 \text{ \AA}. \quad (2.3)$$

The energy expectation value is calculated using a Slater-Jastrow wave function  $\psi_{SJ}$

$$\psi_{SJ} = F\phi = \left( \prod_{i < j} f_{\alpha\beta}(r_{ij}) \right) \mathbf{A} \left( \prod_{j=1}^{N_F} e^{i\vec{k}_j \cdot \vec{r}_j} \xi(m_j) \right), \quad (2.4)$$

where  $\phi$  is a Slater determinant of plane waves and spin functions,  $\xi$  ( $\mathbf{A}$  is the antisymmetrizer for the  $N_F$  fermion labels), and the pair function  $f_{\alpha\beta}$  is written in parametric form:

$$f_{\alpha\beta}(r) = e^{u_{\alpha\beta}(r)/2} = e^{-(b_{\alpha\beta}\sigma/r)^{5/2}}, \quad (2.5)$$

with  $b_{\alpha\beta}$  a variational parameter. In principle we can choose a different  $b$  for each type of pair; however, after investigating this point in detail,<sup>13</sup> we found that in those mixtures where the potentials have the same "core" sizes,  $\sigma_{\alpha\beta}$ , one achieved a negligible reduction in energy by using the pair-dependent  $f_{\alpha\beta}$ . Thus all of the calculations discussed in this paper use  $b_{\alpha\beta} = b$ . Calculating the expectation value of the Hamiltonian, Eq. (2.1), we find

$$E = (1-x)^2 E_{BB}(x) + 2x(1-x) E_{BF}(x) + x^2 \left( E_{FF}(x) + \sum_{F=1}^{N_F} E_F(x) \right), \quad (2.6)$$

where  $x = N_F/N$  is the fermion concentration

$$E_{\alpha\beta}(x) = \frac{1}{2} \rho \int g_{\alpha\beta}(r) \tilde{V}_{\alpha\beta}(r) d\vec{r} \quad (2.7)$$

and

$$\tilde{V}_{\alpha\beta}(r) = V_{\alpha\beta}(r) - \frac{\hbar^2}{4m_{\alpha\beta}} \nabla^2 u_{\alpha\beta}(r). \quad (2.8)$$

In Eq. (2.7)  $\rho$  is the  $d$ -dimensional number density,  $g_{\alpha\beta}(r)$  is a mixed two-particle radial distribution function defined by<sup>8</sup>

$$g_{\alpha\beta}(r_{ij}) = \frac{N_\alpha(N_\beta - \delta_{\alpha\beta})}{\rho_\alpha \rho_\beta l} \int |\psi_{SJ}|^2 d\vec{r}_{(i,j)}, \quad (2.9)$$

where  $\rho_\alpha$  is the partial density of species  $\alpha$ ,  $l$  is the normalization integral, and the notation in the integrand indicates that  $i$  and  $j$  are not to be integrated over, where  $i \in \{\alpha\}$  and  $j \in \{\beta\}$ . Thus  $g_{\alpha\beta}(r_{ij})$  is a measure of the probability of finding particle  $j$  of species  $\beta$  a distance  $r_{ij}$  from particle  $i$  of species  $\alpha$  which is known to be at the origin. In Eq. (2.8) we have defined

$$\frac{1}{m_{\alpha\beta}} = \frac{1}{2} \left( \frac{1}{m_\alpha} + \frac{1}{m_\beta} \right), \quad (2.10)$$

and we have retained a generalization notation with type labels on the potential and pair function. The terms labeled  $E_F(x)$  in Eq. (2.6) are the cluster-

expansion form of part of the kinetic energy,

$$x^2 \sum_{F=1}^{N_F} E_F(x) = \frac{\hbar^2}{4m_F N} \sum_{i=1}^{N_F} \left[ k_i^2 + \frac{1}{I} \int F^2(\vec{\nabla}_i \phi^* \cdot \vec{\nabla}_i \phi) d\vec{\Gamma}^N \right]. \quad (2.11)$$

The radial distribution function  $g_{\alpha\beta}$  and the kinetic energy contributions of Eq. (2.11) are evaluated by means of the statistical cluster expansion introduced by Wu and Feenberg.<sup>15</sup> Thus, we can formally write the  $g_{\alpha\beta}$  in the form

$$g_{\alpha\beta}(r) = g_{\alpha\beta}^B(r) + \Sigma_{\alpha\beta}(r), \quad (2.12)$$

where  $g_{\alpha\beta}^B(r)$  is generated by the "Jastrow" part of the wave function,  $F^2$  only, and  $\Sigma_{\alpha\beta}$  represents the "statistical" contributions. Each  $g_{\alpha\beta}(r)$  has a cluster expansion with statistical contribution because any two particles can interact indirectly through two or more fermions.

In this paper we have truncated the expansions in Eqs. (2.11) and (2.12) after two-body exchange. Thus we have

$$g_{BB}(r) = g^B(r), \quad g_{BF}(r) = g^B(r), \quad (2.13)$$

$$g_{FF}(r) = g^B(r) \left( 1 - \frac{1}{\nu} I^2(k_{FF}r) \right),$$

where we have omitted the type indices on the  $g_{\alpha\beta}^B$  since we only use a single  $b$ ,  $\nu$  is the number of equally populated Fermi seas, and

$$I(k_{FF}r) = \frac{\nu}{N_F} \sum_{i=1}^{N_F} e^{i\vec{k}_i \cdot \vec{r}}, \quad (2.14)$$

where  $k_F$  is the Fermi momentum and the sum depends on whether  $d=2$  or  $3$ . Similarly, for Eq. (2.11),

$$E_1(x) = \frac{\hbar^2}{2m_F N} \sum_{i=1}^{N_F} k_i^2, \quad (2.15)$$

and

$$E_2(x) = E_1(x) \frac{1}{(2\pi)^d} \times \int d\vec{x}_1 \int d\vec{x}_2 x_{12}^2 [S^B(k_{FX_{12}}) - 1], \quad (2.16)$$

where  $S^B(k)$  the liquid structure function, is the Fourier transform of  $g^B(r)$  and the integrals are taken over unit circles ( $d=2$ ) or unit spheres ( $d=3$ ). Three-body exchange could also be included, however, we found that its contribution to the energies

does not affect the basic qualitative behavior which we are trying to describe.

We have chosen to use the hypernetted chain (HNC) approximate integral equation to relate  $u(r)$  to  $g^B(r)$ . The integral equation approach to finding  $g(r)$  is of computational importance because the extreme precision with which this equation can be solved allows us to assess the small "excess" energies which determine the mixture ground state. The solution of the HNC equation and its application to liquid helium is discussed in Ref. 16.

If the liquid phase separates, the two phases will be at the same pressure. Thus it is convenient to use the enthalpy  $H$  to describe the systems,

$$H(x, P) = E(x, \rho) + \frac{P(x, \rho)}{\rho}, \quad (2.17)$$

where  $P$  is the pressure. In order to implement this Legendre transform we need to be able to calculate the pressure accurately. It has been shown<sup>16</sup> that the virial theorem pressure is identical to the "thermodynamic" pressure,  $\rho^2(\partial E/\partial \rho)_x$ , for a pair function of the form of Eq. (2.5) at the variational minimum,  $(\partial E/\partial b)_{\rho, x} = 0$ . Thus we have

$$P = \frac{2}{3} (\epsilon_{KE} - 3\epsilon_6 + 6\epsilon_{12}), \quad (2.18)$$

where the  $\epsilon$ 's are the constituents of the energy,  $E = \epsilon_{KE} - \epsilon_6 + \epsilon_{12}$ . Once the enthalpy as a function of  $x$  and  $P$  is known, the chemical potentials can be immediately obtained from

$$\mu_\alpha = H + x_\beta \left( \frac{\partial H}{\partial x_\alpha} \right)_\rho, \quad (2.19)$$

The chemical potentials as function of  $x$  and  $P$  are the direct route to mixture information since regions of negative concentration gradient signal material instability and phase separation. Thus  $u \rightarrow g \rightarrow E \rightarrow H \rightarrow \mu$  and  $\mu(x, P)$  is examined to learn about the mixtures.

### III. ISOTOPIC BINARY FERMION-BOSON MIXTURES

In order to treat arbitrary (Lennard-Jones) fermion-boson mixtures we shall introduce a scaled set of units such that lengths are measured in units of  $\sigma$  and energies are measured in units of  $\epsilon$ . The first application of this idea to quantum systems was made by de Boer and co-workers<sup>17</sup> and is known as the quantum theorem of corresponding states. If we denote scaled quantities by an asterisk then the enthalpy can be written:

$$H^*(P^*, x; \eta_B, \eta_F) = \frac{H}{\epsilon} = E^* + \frac{P^*}{\rho^*}, \quad (3.1)$$

where  $\eta_B$  and  $\eta_F$  are de Boer parameters and are de-

finied by

$$\eta_\alpha = \frac{\hbar^2}{m_\alpha \epsilon \sigma^2} ; \quad (3.2)$$

we have also used  $P^* = P \sigma^d / \epsilon$  and  $\rho^* = \rho \sigma^d$ . The beauty of Eq. (3.1) is that by calculating  $H^*$  as a function of  $P^*$  and  $x$  for various values of  $\eta_B$  and  $\eta_F$  one can effectively examine the ground-state configuration of *all* isotopic Lennard-Jones fermion-boson mixtures. (In Table I we show the values of  $\eta$  for the helium and hydrogen isotopes.) We now define a concentration-dependent de Boer parameter,  $\eta_x$ ,

$$\eta_x = (1-x)\eta_B + x\eta_F . \quad (3.3)$$

If we were describing an isotopic binary boson mixture then  $\eta_x$  would contain all of the *explicit* concentration dependence of the enthalpy. However in the present case the statistical correlations in the fermion component contribute a further explicit  $x$  dependence. Nevertheless, for our purposes the importance of Eq. (3.3) is that it is a *linear* relationship between  $\eta_x$  and  $x$  (this is only true for an isotopic mixture<sup>13</sup>) so that concentration derivatives are proportional to  $\eta$  derivatives.

We now need to consider the isotopic boson-boson mixture. The ground state of this mixture is *complete* phase separation. This result was obtained by Chester<sup>18</sup> using a perturbation expansion of the partition function. It is supported by detailed numerical calculations<sup>13</sup> on various boson-boson mixtures similar to the calculation described in Sec. II. Here we shall argue for this result. Consider the second concentra-

tion derivative of the enthalpy<sup>13</sup>

$$\left( \frac{\partial^2 H}{\partial x_2^2} \right)_P = - \left( \frac{\Delta m}{1 + x_2 \Delta m} \right) \frac{\partial}{\partial x_2} (\langle V \rangle + P \Omega)_P , \quad (3.4)$$

where the boson isotopes are labeled 1 and 2,  $\Delta m \equiv m_1/m_2 - 1$ ,  $\langle V \rangle$  is the potential energy, and  $\Omega$  is the volume per particle. Let us examine the case  $m_1 > m_2$ . Then increasing  $x_2$  moves us from a heavy-mass system to a light-mass system. However, since both the potential energy and the volume per particle are monotonically decreasing functions of mass,<sup>19</sup> the derivative on the right-hand side of Eq. (3.4) is positive semidefinite. Thus  $H$  is a concave function of  $x$  and the system completely phase separates.

We can thus draw the general conclusion: (a) *boson-boson isotopic mixtures completely phase separate* and the corollary (b) *fermion statistics are a necessary condition for miscibility in the ground state of isotopic fermion-boson solutions*.

Let us now investigate how the fermion nature of a constituent can induce mixing. We can imagine the mixture process occurring in two steps. In step I, we have an isotopic mixture of heavy and light *bosons*, the "underlying" boson system. We know that the ground state of this system is complete phase separation. In step II, we take the light-mass system and "turn on" its Fermi-Dirac nature. Operationally this means that we can regard the  $N_L$  light-mass atoms (the fermions) as having a variable number of spin degrees of freedom. The light-mass system is a boson system when the number of spin degrees of free-

TABLE I. The de Boer parameter  $\eta$  for various substances (H $\uparrow$ , D $\uparrow$ , and T $\uparrow$  denote spin-polarized hydrogen, deuterium, and tritium, respectively). Also given are the masses, coupling constants  $\epsilon$ , "core diameters"  $\sigma$ ,  $\epsilon/\sigma^3$ , and  $N_0\sigma^3$ . We used  $\hbar = 1.05430 \times 10^{-27}$  erg sec and  $N_0 = 6.02252 \times 10^{23}$  particles/mole.

Substance	$m$ (amu) <sup>a</sup>	$\epsilon$ (K) <sup>b</sup>	$\sigma$ (Å)	$\epsilon/\sigma^3$ (atm)	$N_0^3$ (cm <sup>3</sup> / mole)	$\eta$
H $\uparrow$	1.008	6.46	3.69	17.5	30.2	0.547
D $\uparrow$	2.014	6.46	3.69	17.5	30.2	0.274
<sup>3</sup> He	3.016	10.22	2.556	83.39	10.06	0.2409
T $\uparrow$	3.016	6.46	3.69	17.5	30.2	0.183
<sup>4</sup> He	4.003	10.22	2.556	83.39	10.06	0.1815
<sup>6</sup> He	6.019	10.22	2.556	83.39	10.06	0.1207
H <sub>2</sub>	2.016	37.0	2.92	202.5	15.0	0.0763
D <sub>2</sub>	4.028	37.0	2.92	202.5	15.0	0.0382
Ne	20.18	35.6	2.74	235.8	12.4	0.0085
A	39.95	120.0	3.41	412.3	23.9	0.00088

<sup>a</sup>1 amu =  $1.66024 \times 10^{-24}$  g.

<sup>b</sup> $k_B = 1.38054 \times 10^{-16}$  erg/particle K.

dom is  $N_L$  and each light atom has its own Fermi sea.<sup>20</sup> Thus, "turning on the Fermi statistics" means we decrease the number of spin degrees of freedom and the number of equally populated Fermi seas,  $\nu$ , from  $\nu = N_L$  to 2. In Fig. 1 we illustrate schematically the two steps of the mixture process. The boson-boson mixture completely phase separates as shown by the dashed line, its convex envelope. The dot-dashed line, the extrapolation of  $(\partial H/\partial x)_{x_L=0}$ , intercepts the  $x_L = 1$  axis at  $\mu_F(x_L=0)$ —the zero-concentration fermion chemical potential. We denote this point by  $\mu_F(0)$ . [The value of  $\mu_F(0)$  is independent of the statistics of the light-mass constituents because the derivative  $(\partial H/\partial x)_P$ , as  $x \rightarrow 0$ , is a single-particle property of the system.] On Fig. 1 we also show the change in the chemical potential of the light-mass, boson system that follows upon turning on the fermion statistics. Note the arrow on the right-hand axis pointing from  $H_B(1)$  to  $H_F(1)$ , i.e., from  $H_B(1)$ , the value of the light-mass, boson system's chemical potential, to  $H_F(1)$ , the value of the light-mass, fermion system's chemical potential. In this

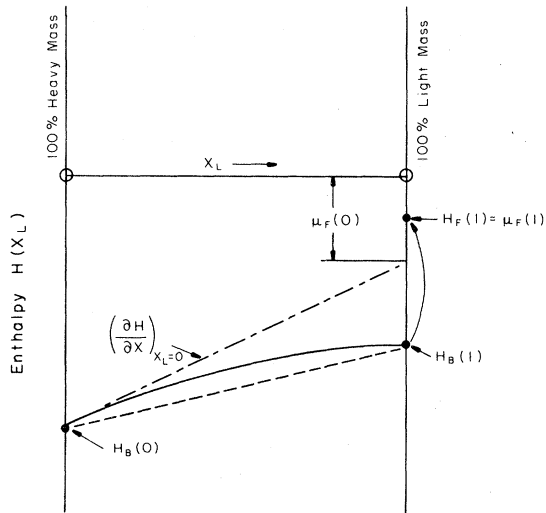


FIG. 1. Schematic plot of enthalpy vs concentration. The solid line shows the enthalpy of an isotopic binary boson mixture. The boson-boson mixture completely phase separates as shown by the dashed line, its convex envelope. The dot-dashed line, the extrapolation of  $(\partial H/\partial x_L)_{x_L=0}$ , intercepts the  $x_L = 1$  axis at  $\mu_F(x_L=0)$ —the zero-concentration fermion chemical potential. We illustrate here a case in which turning on the fermion statistics in the light-mass system produces some mixing since  $\mu_F(1) > \mu_F(0)$ .

figure we have illustrated the case in which turning on the fermion statistics results in a chemical potential,  $\mu_F(1) = H_F(1)$ , that is greater than  $\mu_F(0)$ . A given mixture system can be characterized by the relative size of  $\mu_F(1)$  and  $\mu_F(0)$  [or  $(\partial H/\partial x)_{P,x=0}$ ]. If  $\mu_F(1) < \mu_F(0)$  the enthalpy must bend downward as  $\mu(x)$  evolves from  $\mu_B(0)$  to  $\mu_F(1)$  and there must be some phase separation. The zero-concentration enthalpy second derivative is always positive because it is dominated by the Fermi kinetic energy; thus, if  $\mu_F(1) > \mu_F(0)$  then there must be some mixing.<sup>21</sup> We are thus led to the condition  $\mu_F(1) = \mu_F(0)$  as separating those systems in which there must be mixing from those systems in which there must be separation. Below we shall show through detailed numerical calculations that, in fact, all systems for which  $\mu_F(1) < \mu_F(0)$  completely phase separate.

In the discussion above we chose  $H_F(1) > H_B(1)$ . In our numerical studies of boson and fermion systems we always obtained  $H_F(1) > H_B(1)$ . We are unable to find any counterexamples. In addition there are several models in which this behavior can be exhibited analytically (e.g., hard-sphere fermions and a Stoner model). Furthermore, if one makes an expansion of the energy, Eq. (2.6), in powers of  $1/\nu$  then one can show that the derivative  $(\partial E/\partial \nu)$  in the neighborhood of  $1/\nu = 0$  is always positive.

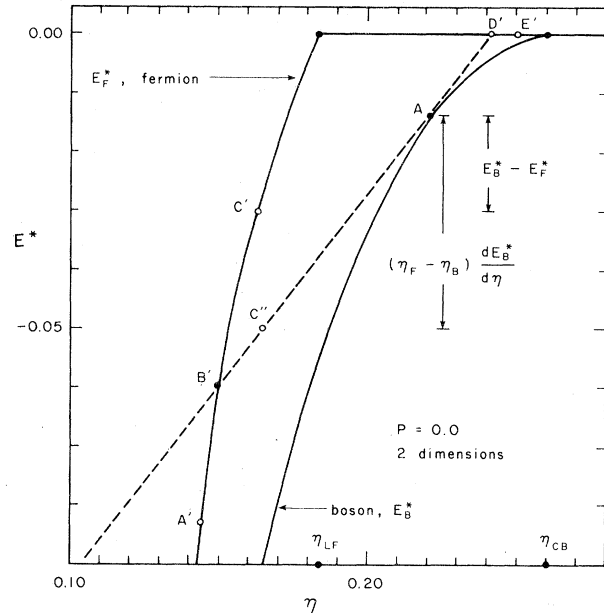


FIG. 2. Reduced boson and fermion energies as functions of  $\eta$  for 2D systems at zero pressure. The fermion energy intercepts (points  $B'$  and  $D'$ ) of a tangent to the boson energy curve (at the point  $A$ ) represent the places where  $\mu_F(0) = \mu_F(1)$  and thus correspond to the limits of systems which are miscible in the boson system at zero pressure (see text). Therefore fermion systems  $A'$  and  $E'$  show complete phase separation while fermion system  $C'$  is partially mixed.

We shall now introduce a simple construction whereby one may find all systems satisfying the equality  $\mu_F(1) = \mu_F(0)$  from a knowledge of the behavior of the pure boson and pure fermion systems. Using Eq. (3.3) in Eq. (2.19) we find

$$\mu_F^* = H^* + (\eta_F - \eta_x) \left( \frac{\partial H^*}{\partial \eta_x} \right)_{P^*} \quad (3.5)$$

Thus,  $(\partial H^*/\partial \eta_x)_{P^*}$  contains the same information as  $(\partial H/\partial x)_P$ . The condition  $\mu_F(1) = \mu_F(0)$  thus corresponds to  $\mu_F^*(\eta_F) = \mu_F^*(\eta_B)$  and yields

$$\left( \frac{\partial H_B^*}{\partial \eta_x} \right)_{P^*} = \left( \frac{H_F^* - H_B^*}{\eta_F - \eta_B} \right) \quad (3.6)$$

This equation embodies the geometrical statement that a tangent through the boson enthalpy curve at the point  $(\eta_B, H_B^*)$  should intercept the fermion enthalpy curve at the point  $(\eta_F, H_F^*)$ . In Fig. 2 we show a plot of  $E_B^*$  and  $E_F^*$  as functions of  $\eta$  (for  $d=2$  and  $P=0.0$ ). A tangent has been drawn through a point on the boson curve labeled *A* which intercepts the fermion curve at points *B'* and *D'*. From the above discussion we can predict that a fermion sys-

tem with an  $\eta$  between that of systems *B'* and *D'*, such as point *C'*, must show some mixing whereas a fermion system with an  $\eta$  outside of this region, such as *A'* or *E'*, must show separation.

In Fig. 3, we show the results of the numerical analysis of the ground state of a large number of  $d=2$  isotopic boson-fermion mixtures as described in Sec. II. On the  $(\eta_B, \eta_F)$  plane, where we can locate all boson-fermion mixtures, we show numbers that correspond to the maximum solubility of fermions in bosons at  $P=0.0$ . We note that there are two regions in the figure in which the fermions are completely immiscible in the bosons. *The boundaries of these regions correspond exactly to those obtained from the construction shown in Fig. 2 and described above.* Thus examining boson system *A* of Fig. 2

( $\eta_B=0.22$ ), we indeed see that mixtures with fermion systems *A'* and *E'* completely phase separate, a mixture with fermion system *C'* shows mixing, and mixtures with *B'* and *D'* are on the complete separation border. We may thus conclude that *the locus of systems obeying  $\mu_F(0) = \mu_F(1)$  separates those mixtures whose ground state is complete separation from those mixtures whose ground state is at least partially mixed.*

The de Boer parameter  $\eta$  is a rough measure of the

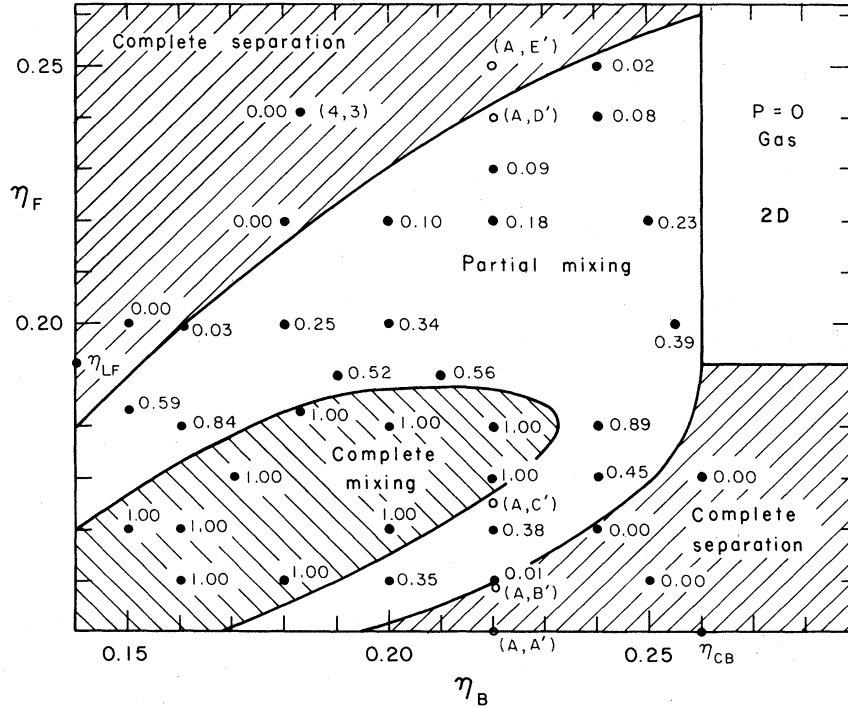


FIG. 3. Maximum fermion solubilities in  $(\eta_B, \eta_F)$  space on the  $P=0.0$  plane for isotopic mixtures in  $d=2$ . The boundaries separating those mixture systems with zero solubility from those systems with finite solubility were obtained from the construction of Fig. 2. The points labeled  $(A, A')$ ,  $(A, B')$ , etc., correspond to those same points in Fig. 2. The point labeled  $(4,3)$  is  ${}^3\text{He}-{}^4\text{He}$  which, in 2D, completely phase separates. The points on the axes labeled  $\mu_{CB}$  and  $\mu_{LF}$  are the largest values of  $\eta$  for which boson and fermion systems, respectively, have many-body bound states (see text).



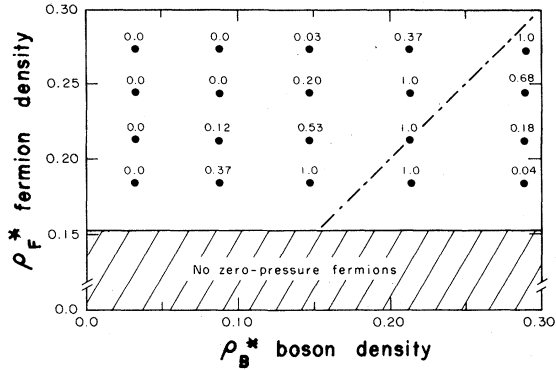


FIG. 5. Maximum fermion solubilities for  $d=3$  fermion-boson mixtures as a function of  $\rho_F^*$  and  $\rho_B^*$ , the reduced densities of the pure phases. This figure shows the correlation between large miscibility and equal volumes per particle since the systems which exhibit complete mixing are clustered around the diagonal (dot-dashed line).

ing it is a property of isotopic mixtures and not necessarily mixtures in general: it is simple to conceive of mixtures whose pure phases have identical volumes per particle and yet completely phase separate.<sup>13</sup>

#### IV. $^3\text{He}$ - $^4\text{He}$

We shall begin this section by discussing  $^3\text{He}$ - $^4\text{He}$  mixtures in two dimensions. In Fig. 3 we showed that at zero pressure the mixture is completely phase separated. From our discussion in the previous section we can conclude that this is due to the *gaseous* ground state of  $(d=2)^3\text{He}$ . This result plus the finite pressure behavior had previously been considered<sup>24</sup> as a model of the physisorbed  $^3\text{He}$ - $^4\text{He}$  system studied by Hickernell, McLean, and Vilches<sup>25</sup> (HMV). The prediction of phase separation in the mixture ground state is not clearly supported by the (specific-heat) data of HMV. By invoking the recent work of Carlos and Cole,<sup>26</sup> and Wang, Senbetu, and Woo,<sup>27</sup> it may be possible to understand the complicated system studied by HMV. Carlos and Cole, by analyzing He scattering experiments from a graphite surface, were able to determine an empirical graphite-He potential function. This potential permits more substrate normal motion than the previous potentials and also enhances the effects of the periodic maxima and minima. Using this potential, Wang, Senbetu, and Woo found that the epitaxial solid phase was energetically favored over a fluid ground state. It thus appears likely then, that HMV were studying a sublimation like coexistence between gaseous and registered solid phases and not a liquid mixture.

In Fig. 4 we showed the  $P=0$  maximum fermion

solubilities for  $d=3$  mixtures. In addition to  $^3\text{He}$ - $^4\text{He}$ , we also labeled the positions of the spin-polarized hydrogen mixtures ( $\text{T}\uparrow, \text{D}\uparrow$ ) and ( $\text{H}\uparrow, \text{D}\uparrow$ ). We note that these results are for  $\nu=2$  Fermi seas; however, deuterium has a spin-one nucleus and can therefore populate  $\nu=3$  Fermi seas. Thus although Fig. 4 indicates that both ( $\text{T}\uparrow, \text{D}\uparrow$ ) and ( $\text{H}\uparrow, \text{D}\uparrow$ ) completely phase separate, this statement can be made with confidence only for the latter system.

At zero pressure, Fig. 4 shows that the calculated maximum  $^3\text{He}$  solubility is 0.18, a factor of three larger than experiment.<sup>28</sup> Nevertheless, the *qualitative* physics is correct:  $^3\text{He}$  has a small solubility in  $^4\text{He}$  at zero pressure. Indeed in this section we shall show that the simple calculational method discussed in Sec. II can be employed to satisfactorily obtain a number of ground-state properties of the mixture.

In Fig. 6 we plot the maximum  $^3\text{He}$  solubility as a function of pressure. The theoretical results are compared to the experimental data of Watson, Repy, and Richardson,<sup>29</sup> the results for a hard sphere  $^3\text{He}$ - $^4\text{He}$  mixture (in lowest order) and an alternative cluster expansion (to be discussed below). The outstanding feature in the theoretical results is the maximum in the maximum solubility which occurs at  $\sim 4$  bars. This behavior is also present in the experimental data but in a more subdued manner. A qualitative explanation of this behavior can be made in terms of the underlying (in the sense of the discussion in Sec. III) boson-boson mixture. As the pressure is increased the "statistical" part of the energy, which crudely goes like  $\rho^{2/3}$ , becomes relatively less

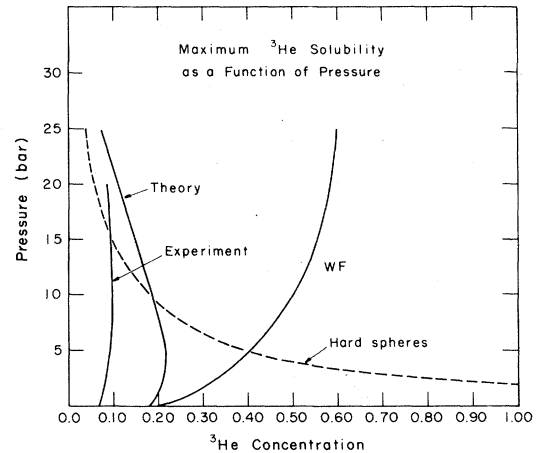


FIG. 6. Maximum  $^3\text{He}$  solubility as a function of pressure. The experimental data are from Ref. 29. The line labeled theory is the result from the procedure of Sec. II. The line labeled WF is an alternative cluster expansion (see text) and the dashed line is the result for hard spheres in lowest order. The maximum in the maximum solubility is explained by appeal to the model of the "underlying" boson-boson mixture.



important than the "interaction" part, which crudely goes like  $\rho$ . Thus as the pressure is increased the mixture tends towards its underlying boson-boson mixture whose ground state is complete separation. This behavior can be seen analytically in the hard-sphere mixture (dashed line in Fig. 6). For this system there is a lower critical pressure<sup>4</sup> below which there is complete mixing and above which the system increasingly separates due to the decreasing relative importance of the Fermi statistical constituents in the energy. However, as discussed by van Leeuwen and Cohen,<sup>4</sup> the very large compressibility in the hard sphere system makes it difficult to map quantitatively onto real  $^3\text{He}$ - $^4\text{He}$ . The influence of fermion statistics can also be gauged by examining the quantity  $\mu_{3F}(1) - \mu_3(0)$  as a function of pressure. This is shown in Fig. 7 along with the maximum solubility (dashed line) and the quantity  $\mu_{3B}(1) - \mu_3(0)$  (triangles) where  $\mu_{3B}(1)$  is the chemical potential of a pure boson  $^3\text{He}$  system. Because  $\mu_3(0)$  is independent of the statistics of the mass-3 constituent, the

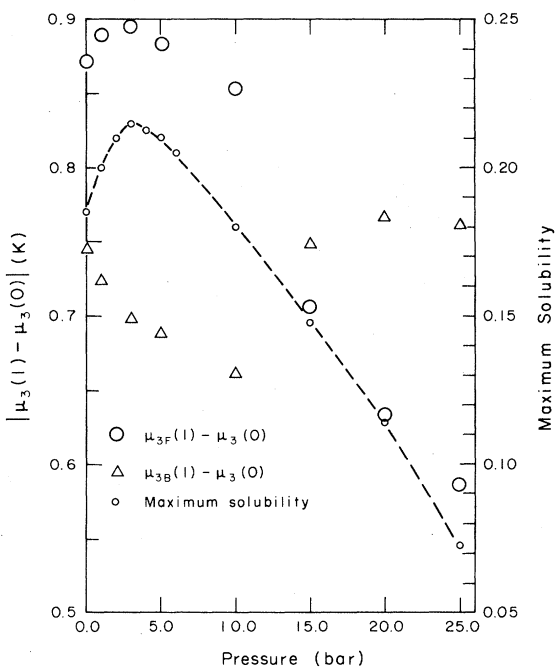


FIG. 7. Chemical potential differences and  $^3\text{He}$  maximum solubility as a function of pressure. The maximum solubility (dashed line) is drawn against the right-hand ordinate. The circles represent the difference  $\mu_{3F}(1) - \mu_3(0)$  where  $\mu_{3F}(1)$  is the pure fermion  $^3\text{He}$  chemical potential. The triangles represent the difference  $\mu_{3B}(1) - \mu_3(0)$ , where  $\mu_{3B}(1)$  is the pure boson chemical potential. The correlation between the circles and the maximum solubility line is evident. This is interpreted as supporting our picture (see Sec. III) relating the cost in energy of Fermi-Dirac statistics to the miscibility.

quantity  $\mu_{3F}(1) - \mu_3(0)$  is a crude measure of the importance of Fermi statistics. The correlation between  $\mu_{3F}(1) - \mu_3(0)$  and the maximum solubility, as shown in Fig. 7, is dramatic. The quantity  $\mu_{3B}(1) - \mu_3(0)$  is qualitatively independent of pressure, however, its behavior appears somewhat erratic.

The relationship between the pure phase quantities  $[\mu_4(0)$  and  $\mu_3(1)]$  and experiment has been considered in detail elsewhere.<sup>16</sup> In Fig. 8 we show the quantity  $\mu_3(0)$  as a function of pressure as calculated here and from the experiments of Edwards and co-workers.<sup>30</sup> The calculated curve is the same monotonic function of pressure as the experimental curve. However, the theoretical value of  $\mu_3$  is 0.8 K too high at zero pressure and approximately 2 K too high at 20 bars.

In Fig. 9 we show the excess volume or BBP<sup>14</sup> parameter  $\alpha$ , defined by

$$x\alpha = -\frac{(\rho(x) - \rho_4)}{\rho_4} \quad (4.1)$$

where  $\rho_4$  is the  $^4\text{He}$  density and  $\rho(x)$  is the density at concentration  $x$  and both are at a given pressure. The experimental data are from Ref. 29. The agreement between theory and experiment is gratifying and shows that the theory gives a reasonable account of the volume excluding short-range order effects. Good agreement between theory and experiment has also been obtained by Massey and Woo<sup>31</sup> and Davison and Feenberg.<sup>32</sup>

In Fig. 10 we compare our calculated (zero-pressure) osmotic pressures with the results of Landau, Tough, Brubaker, and Edwards.<sup>33</sup> Osmotic equilibrium is defined by the equality  $\mu_4(P, x)$

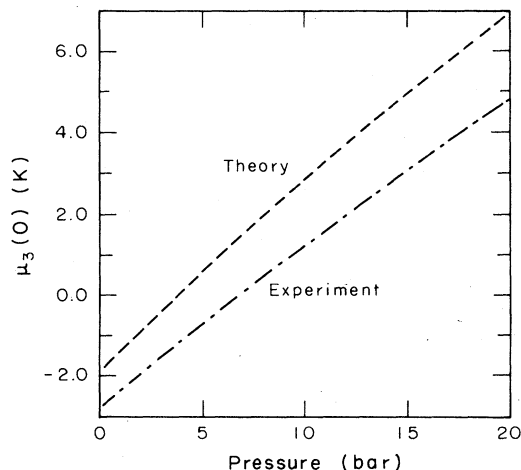


FIG. 8.  $^3\text{He}$  zero-concentration chemical potential as a function of pressure. The curve labeled experiment is a line through the data of Ref. 28.

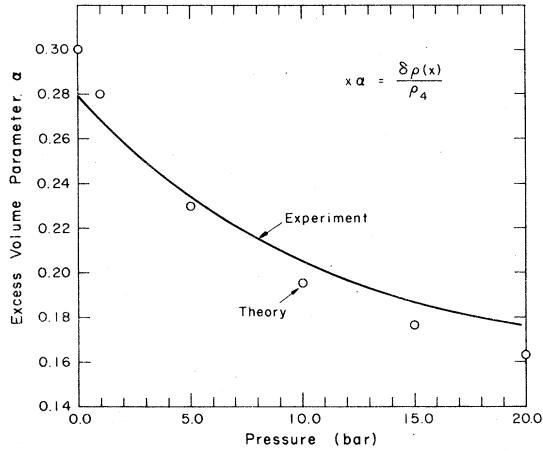


FIG. 9. Excess volume or BBP parameter as a function of pressure. The curve labeled experiment is a line through the data of Ref. 29.

$= \mu_4(P - \pi, 0)$  where  $\pi$  is the osmotic pressure. If we expand the right-hand side about  $P$  we find

$$\pi = \rho_4(P) [\mu_4(P, 0) - \mu_4(P, x)] \quad (4.2)$$

The curve labeled theory was obtained from Eq.

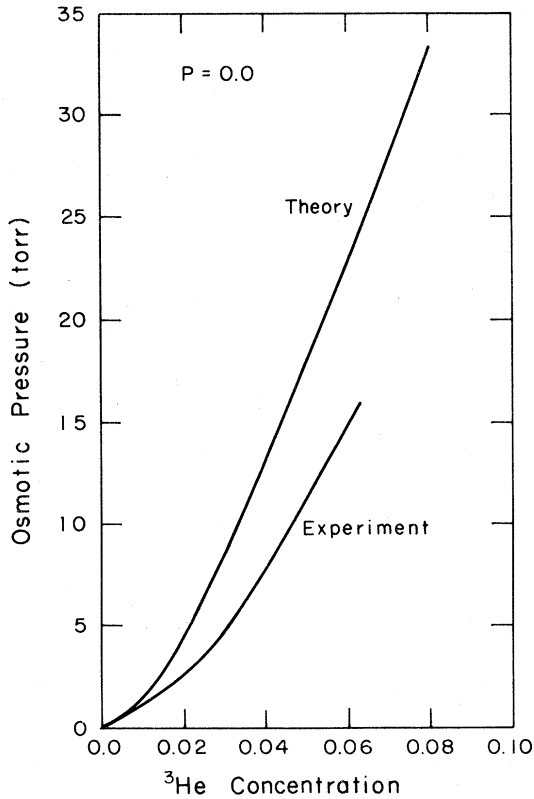


FIG. 10. Osmotic pressure as a function of  $^3\text{He}$  concentration at zero pressure. The curve labeled experiment is a line through the data of Ref. 33.

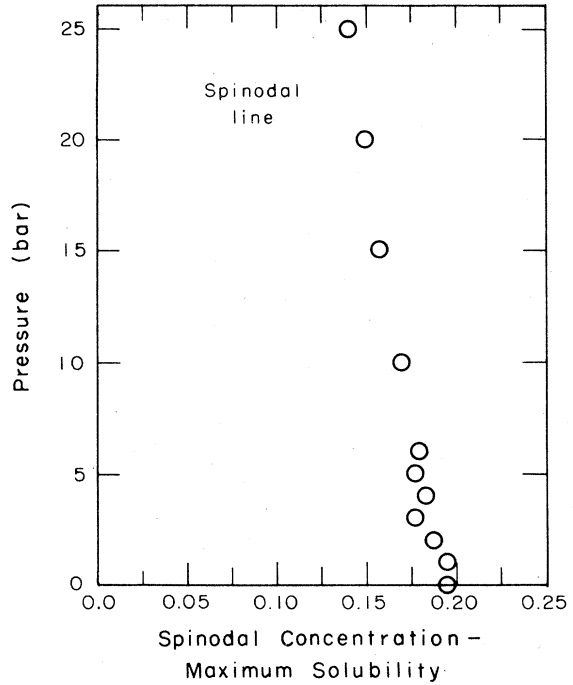


FIG. 11. Position of the spinodal point measured with respect to the maximum solubility as a function of pressure.

(4.2). The calculated osmotic pressure rises too quickly as a function of  $x$ , thus, by  $x \approx 0.05$  the calculated  $\pi$  is 50% larger than the experimental  $\pi$ . We do find that  $\pi(x)$  is only a weak function of  $P$  which is in agreement with experiment.<sup>34</sup>

A mixture is absolutely unstable to phase separation in a region where the enthalpy curvature ( $T = 0$  K) is negative; i.e.,  $(\partial\mu_3/\partial x_3)_P < 0$ . Because of the nature of the "double-tangent" construction,  $(\partial\mu_3/\partial x_3)_P$  is positive at the maximum solubility and for an extensive region beyond. Within this region one

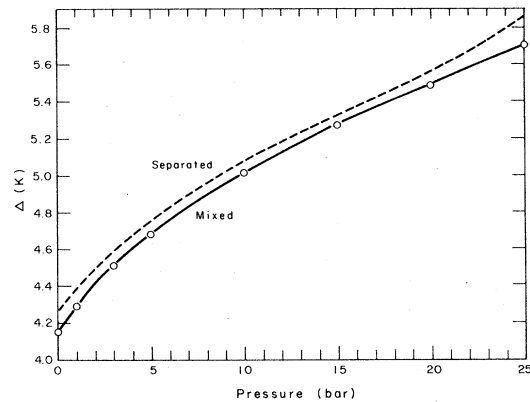


FIG. 12.  $\Delta \equiv \mu_3 - \mu_4$  at the maximum solubility as a function of pressure. The dashed line is the line of spinodal points.

can form homogeneous mixtures in unstable equilibrium: supersaturated solutions. This behavior has been observed in the laboratory.<sup>35</sup> The limiting concentration at which  $(\partial\mu_3/\partial x_3)_P = 0$ , is known as the spinodal point. In Fig. 11 we plot the position of the spinodal point relative to the maximum solubility as a function of pressure. The dependence on pressure is very weak: a line through the points is practically vertical. It is not clear, because of the scatter in the points, whether the spinodal point is at all sensitive to the maximum in the maximum solubility.

The thermodynamic conjugate variable to the  ${}^3\text{He}$  concentration is  $\Delta \equiv \mu_3 - \mu_4 = (\partial H/\partial x)_P$ . In Fig. 12 we plot the position of the phase separation line in terms of the fields  $P$  and  $\Delta$ . The curve is a line of first-order phase transitions and the region below the curve is the homogeneous mixture. The dashed line is the locus of spinodal points.

## V. CONCLUSION

In this paper we have been concerned with trying to discover those aspects of bosons and fermions which are important in determining the mixture ground state. In Sec. III, by examining a general class of mixtures in  $(\eta_B, \eta_F)$  space we were able to construct a picture of the mixing process that permitted us to assess mixture behavior. In order to test this picture we carried out a series of calculations of mixture systems. These calculations give support to the physical picture we have of the important energetics in mixing. In Sec. IV we showed that the computational scheme employed in Sec. III describes the properties of  ${}^3\text{He}$ - ${}^4\text{He}$  mixtures quite well.

In this section we shall discuss some of the approximations that have been used in our calculations and the limitation they place on the significance of our results. Mixtures are more sensitive to calculational details than pure systems because the essential information about the mixture ground state is contained in energy differences, e.g., the enthalpy second derivatives. That is, from a variational perspective, a reasonable enthalpy upper bound does not necessarily imply a reasonable second derivative. Alternatively, it is the excess enthalpy,

$$H_{\text{ex}}(x) \equiv H(x) - [(1-x)H(0) - xH(1)] ,$$

which determines the mixture ground state and in Fig. 13 we show  $H_{\text{ex}}$  at  $P = 0.0$  and  $10.0$  bars for  ${}^3\text{He}$ - ${}^4\text{He}$ . We note that  $|H_{\text{ex}}| \leq 40$  mK which is two orders of magnitude smaller than the enthalpy in the pure phases. The two approximations which we discuss below are the use of a cluster expansion and the use of a single  $u(r)$  for each type of pair.

There are two aspects to the question of the cluster expansion: (a) the effect of truncation and (b) the

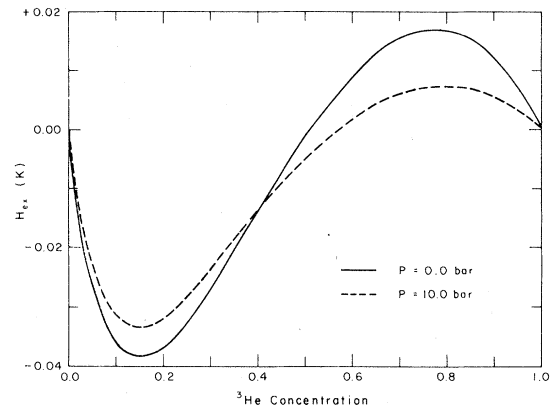


FIG. 13. Excess enthalpy as a function of concentration at  $\rho = 0.0$  and  $10.0$  bars.

use of a particular cluster expansion. We can estimate the effects of truncation by including three-body exchange in the enthalpy. Since this has the effect of *lowering* the  ${}^3\text{He}$  energy (while leaving the  ${}^4\text{He}$  energy unaffected) the maximum solubility decreases. Thus for  ${}^3\text{He}$ - ${}^4\text{He}$  at zero pressure the maximum solubility decreases to 12%. That is, the change is small and in the right direction. In Fig. 6 the line labeled WF is the maximum solubility calculated with the original Wu-Feenberg expansion.<sup>36</sup> That is,  $u(r)$  in Eq. (2.5) is chosen to minimize the energy of a fictitious boson system at the same number density as the fermion system. Clearly the behavior of the maximum solubility is sensitive to the treatment of the fermion statistics. The molecular-dynamics calculations of Hansen and Schiff<sup>7</sup> used this WF cluster expansion; however, they included three-particle exchange. Hansen and Schiff report the *same* sort of monotonically increasing maximum solubility only shifted downward to smaller concentrations. Thus, we find that the effects of truncation are small: lowering the  ${}^3\text{He}$  energy a small amount relative to the  ${}^4\text{He}$ , lowers the maximum solubility. However, the maximum solubility is clearly a *sensitive* test of the particular cluster expansion. An attractive possibility is to generalize the Fermi hypernetted chain integral equation approach for use in the mixtures.

There are two basic ways that one may generalize the simple pair-independent pair factor of Eq. (2.5). First, as indicated in Eq. (2.5), one may include a different  $u(r)$  for each type of pair; second, one may make  $u(r)$  *state* dependent so that it correlates spin-parallel pairs of fermions differently than spin-antiparallel pairs. The simple Slater-Jastrow wave function of Eq. (2.4) is the more or less conventional approach to the boson or fermion ground state. One can generalize this by including various projection

operators in the Jastrow part, by considering a linear combination of Slater determinants by using Feenberg functions (three- or more-body correlations) instead of the simple Jastrow function, etc. The basic rules, however, are: (i) by lowering the fermion energy relative to the boson energy the maximum solubility is decreased and (ii) by lowering the energy of the mixture relative to the pure phases, the maximum solubility increases. The effects of generalizing  $u(r)$  to a pair-dependent form have been tested quantitatively for the zero-concentration chemical potentials<sup>13</sup> where it was found, for example, that the more general wave function lowered  $\mu_3(0)$  by only 2–3%. We thus believe that although more complicated wave functions may change the boundaries of Figs. 3 and 4 quantitatively the essential physics has been found and understood. In summary, then, our basic conclusions from Sec. III are (i) Fermi-Dirac

statistics in at least one component are a necessary requirement for miscibility in the ground state of an isotopic mixture. (ii) The locus of systems satisfying  $\mu_F(0) = \mu_F(1)$  separates those mixture systems which completely phase separate from those mixture systems which exhibit at least partial mixing in the general  $(\eta_B, \eta_F)$  space. (iii) The relative volume per particle of the pure components determines the extent of mixing in isotopic fermion-boson systems.

#### ACKNOWLEDGMENTS

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