$$\left(1-\frac{\rho_g}{\rho_f}\right)J_M = 2\rho_g\left(\frac{m}{2\pi k_B T}\right)^{1/2}\left[\mu_f-\mu_g + \left(s_g-\frac{k_B}{2m}\right)(T_f-T_g)\right], \quad \text{(A7)}$$

$$J_Q = -\frac{\rho_g}{2}\left(\frac{k_B T}{2\pi m}\right)^{1/2}\left[\mu_f-\mu_g + \left(s_g-\frac{9}{2}\frac{k_B}{m}\right)(T_f-T_g)\right], \quad \text{(A8)}$$

to first order in $(T_f - T_g)$ and $(\mu_f - \mu_g)$.

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[*] Research supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-GEN-10, P.A. 11: Report No. UCSD-10P11-68/69-93.

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PHYSICAL REVIEW VOLUME 188, NUMBER 1 5 DECEMBER 1969

Low-Temperature Density and Solubility of He^3 in Liquid He^4 under Pressure*

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(Received 28 July 1969)

The molar volumes of liquid mixtures of He^3 in He^4 up to 10 molar % have been measured to 22 atm pressure and to 50 mK using a dielectric technique. The single-phase measurements provide a determination of the Bardeen-Baym-Pines (BBP) parameter α under pressure. A weaker pressure dependence is found than in the measurements of Boghosian and Meyer. The ground-state kinetic energy for pure He^4 is deduced from α. The two-phase measurements indicate that the solubility at 50 mK of He^3 in He^4 rises from $(6.6 \pm 0.1)\%$ at $P=0$ to a maximum of $(9.5 \pm 0.12)\%$ at 10 atm; it then drops to $(8.3 \pm 0.14)\%$ at 22.5 atm. This behavior is found to be consistent with the BBP effective interaction theory using the Ebner potential.

I. INTRODUCTION

In this experiment, we have measured the molar volumes of dilute mixtures of He^3 in He^4 and of pure He^4 at pressures above the saturated vapor pressure and at temperatures down to 50 mK. The molar volumes are determined by measuring the dielectric constant of the helium with a capacitor which is part of an oscillator tank circuit. We then use these molar volumes to determine the solubility of He^3 in He^4 at 50 mK and the relative excess volume of He^3 in He^4 at pressures up to 22 atm. The latter differs considerably from the measurement of Boghosian and Meyer.[1]

Dilute mixtures of He^3 in He^4 have been the subject of very intense study, both experimentally and theoretically, in the last five or ten years. There are now several sources that review the properties of dilute mixtures,[2,3] so that we shall only give a brief introductory description in this paper.

Below 0.5 K, liquid He^4 is almost completely in its quantum-mechanical ground state. There are almost no real roton or phonon excitations. He^3 atoms have the same electronic structure as He^4, therefore one might expect that He^3 impurities in He^4 at these temperatures would behave like independent particles. This is the basis of the Landau-Pomeranchuk model,[4,5] where the energy-momentum relation of the quasiparticles is given by

$$E = -E_{03} + q^2/2m_0^* . \qquad (1)$$

The energy E_{03} is the binding energy for a single He^3 atom in He^4. The fact that the He^3 atoms have to move through a liquid background rather than vacuum results in the effective mass of the quasiparticles, m_0^* being larger than the atomic mass of the He^3 atoms m_3. Since He^3 is a fermion, the quasiparticles would be expected to obey Fermi statistics and hence be characterized by a degeneracy temperature

$$T_F = \hbar^2(3\pi^2 n_3)^{2/3}/2m_0^* k_B , \qquad (2)$$

where n_3 is the number density of the He^3 atoms in the mixture, and k_B is Boltzmann's constant. For temperatures greater than T_F, the dilute mixtures behave much like a perfect gas; for instance, the specific heat per particle is found to be independent of temperature and equal to $\frac{3}{2}k_B$ per He^3 atom (the He^4 phonon specific heat below 1 K is negligible).[6] At temperatures much less than T_F, one would expect to see degeneracy effects. For most mixtures this is not possible because of phase separation. At low-enough temperatures, the He^3 "gas" condenses into an almost pure phase which because of its smaller density, floats above the He^4. Fortunately, however, this is not true for all mixtures. For mixtures with molar concentration less than about 6.4%, no phase separation takes place,[7,8] and hence these mixtures can be studied at very low temperatures.[9] This result is also important in the design of the continuous He^3-He^4 dilution regrigerator.[9,10]

Many of the properties of dilute mixtures are successfully explained in terms of the phenomenological theory of Bardeen, Baym, and Pines (BBP).[11] They start with (1), but consider also the effects of weak interactions between the He^3 quasiparticles. (The interaction energy considered is only that part of the bare particle-interaction energy that is different when He^3 atoms are replaced with He^4 atoms. Because He^3 and He^4 are isotopes, this difference is weak, whereas the bare particle interaction due to van der Waals forces between the atoms is strong.) An interesting result of BBP's analysis is that the scale of the interaction is determined by the relative difference α in the molar volumes of the He^3 solute atoms and the He^4 atoms. The number α is defined by

$$v_m(x, P, T) = v_4(P, T)[1 + \alpha(x, P, T)x] , \qquad (3)$$

where v_m is the molar volume of a mixture of molar concentration x at pressure P and temperature T, and v_4 is the molar volume of pure He^4. The scale of the interaction energy is given by

$$V_0 = -\alpha^2 m_4 s_4^2/n_4 , \qquad (4)$$

where m_4 is the He^4 mass, s_4 the He^4 first-sound velocity, and n_4 the number density of pure He^4. V_q is the Fourier transform of the real-space interaction potential $V(\vec{r})$. Hence, $V_0 = \int V(\vec{r})d^3\vec{r}$ is a volume average of the potential. It can be shown that the BBP parameter α is related fairly accurately to the ground-state properties of He^4 by

$$\alpha = (\tfrac{1}{3}v_4)\frac{\partial\langle KE\rangle}{\partial P} , \qquad (5)$$

where $\langle KE\rangle$ is the ground-state average kinetic energy of pure He^4.[12]

From our molar-volume data above phase separation, we calculate $\alpha(P)$ and compare it to the previous measurements of Boghosian and Meyer[1] and to several recent theoretical calculations based on (5).[12,13] Ebner[14] has shown that for an effective interaction V_q, the chemical potential for the He^3 atoms in solution is given by

$$\mu_3 = -E_{03} + \mu_f + n_3 V_0 - (4\pi^2\hbar^3)^{-1}\int_0^{2p_f} q^2\left(1 - \frac{q}{2p_f}\right) V_q dg, \qquad (6)$$

at $T = 0$ and $P = 0$. In this equation, μ_f is the chemical potential for an ideal Fermi-Dirac gas with the same number density n_3, and effective mass m_0^*, as the He^3 in the mixture. At finite pressure P, one needs to add the term $\int_0^P(1+\alpha)v_4 dP$.[15] In the presence of the pure He^3 phase, this chemical potential must be equal to $\mu_3{}^0$, the chemical potential of pure He^3. Under pressure, this is

$$\mu_3{}^0 = -L_{03} + \int_0^P v_3 \, dP. \qquad (7)$$

Here L_{03} and v_3 are the latent heat and molar volume of pure He^3. We have used these equations to calculate the maximum solubility of He^3 in He^4 at 0 K and compared this to our experimental results.

II. APPARATUS

The sample chamber containing the measuring capacitor and known mixture was built into a copper block which also contained the mixing chamber of a dilution refrigerator of the Wheatley type.[10]

The sample chamber block is shown in Fig. 1. In the top of the chamber a coil of 44 turns of 0.25-mm niobium wire, 1.11 cm high, and 1.11 cm diam was imbedded in Epibond 100A and packed with cerous magnesium nitrate (CMN). A Robinson oscillator[16] at room temperature operating at a frequency of 3.5 MHz was used to measure the susceptibility of the salt pill, which was used in turn to calibrate the Speer 220 Ω carbon resistor located at the bottom of the chamber. CMN is known to obey Curie's law in the temperature range of this experiment.[17] The carbon resistor was first calibrated against the vapor pressure of pure He^3 in the range 0.5–1.2 K using the T_{62} temperature scale.[18] (The He^3 was contained in a small chamber in the copper block which, for the convenience of drawing, is not shown in Fig. 3.) The Curie constant of the CMN salt pill was found by calibration against the resistor in this temperature range. The inside of the sample chamber was electroplated with tin and the bottom of the salt-pill plug was covered with a tin cap to isolate the salt pill from the rest of the sample chamber. Because of drift in the Robinson oscillator circuit, the Curie constant of the salt pill could only be determined to about ±10%, hence our over-all temperature scale is believed to be correct only to ±10%.

The measuring capacitor at the bottom of the chamber consisted of a solid inner cylinder, 1.26 cm diam by 1.26 cm long, and a concentric outer cylinder machined to give a gap of about 0.13 mm. Both pieces were made of oxygen-free high conductivity copper and were electropolished and electroplated with tin before assembly. The capacitor was assembled by centering the inner cylinder with shim-stock sleeves and then securing it with small beads of Stycast 2850GT epoxy.[19] The capacitor was then attached to the sample-chamber flange with heads of Stycast. This design of locating the capacitor completely inside the sample chamber was to minimize any pressure dependence of the capacitor. For the concentrations used, the phase boundary was always above the capacitor. The capacitor and a 40-turn $\frac{3}{8}$-in.-i.d., coil of No. 25 copper wire formed the tank circuit of a tunnel-diode oscillator. The BD-5 tunnel diode and associated circuitry was thermally grounded at 1.2 K. The oscillator operated at a frequency of 11.5 MHz.

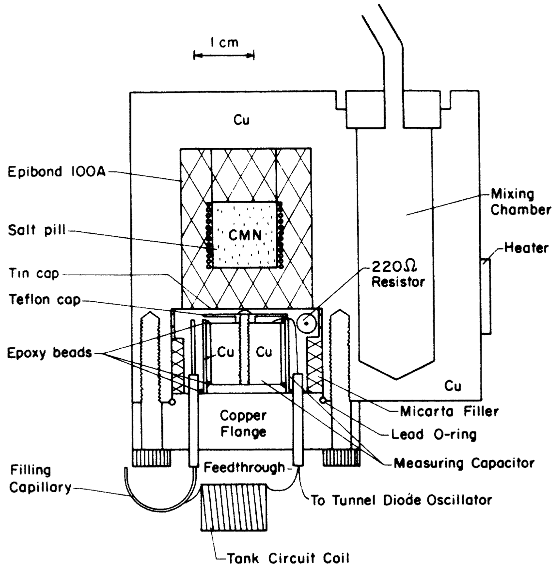

FIG. 1. Sample chamber.

Filling of the mixture was performed through 2 m of 0.102-mm-i.d.×0.79-mm-o.d. Cu-Ni capillary tube. The capillary remaining between still and the bath at 1.2 K and at the still at 0.7 K, with 100 cm of capillary remaining between still and sample chamber. Such small bore capillary is necessary both to minimize the heat leak through the liquid mixture to the sample chamber and to assure that the concentration in the sample chamber is affected very little by the He^3 that enters the chamber from the capillary due to the heat-flush effect. The liquid volume of the sample chamber was 4.8 cm^3. The ratio of capillay to sample-chamber volume was 3.4×10^{-3}.

A mercury piston, driven by hydraulic oil, was used to pressurize the mixture. Pressure in the sample chamber was measured with a specially designed capacitive transducer located at room temperature. The capacitor in the gauge, along with a coil, formed the tank circuit of another tunnel-diode oscillator similar to the one used for the sample chamber. At $P=0$ atm, the output frequency was 17 MHz with a sensitivity of 7 kHz/ψ, increasing to a sensitivity of 22 kHz/ψ at 20 atm. The gauge was calibrated periodically with a Mansfield-Green–type WG deadweight tester. Pressure could be measured to an accuracy of ±0.02 atm.

Each He mixture was made with a Toepler pump system and a cathetometer to an accuracy of about 0.01% in molar concentration, and stored at 1 atm in 8.3-liter metal tanks.

III. PROCEDURE AND DATA ANALYSIS

A. Experimental Procedure

To begin each experiment, the sample chamber was cooled to about 0.3 K. The mixture was then filled into the sample chamber from the pressure system at 30–50 ψ pressure. Filling continued un-

until the sample-chamber oscillator frequency stopped changing. This indicated the capacitor and its fringing field were filled with liquid. Filling took 2 or 3 h. After filling, the sample chamber was cooled to 50 mK. On some runs, the cooling was stopped at a number of points in order to trace out the saturated-vapor-pressure phase diagram. At 50 mK, more sample was introduced to compress to 22 atm, points being taken every 25ψ. Except for some cases mentioned later, data points were taken only after the temperature, sample-chamber oscillator frequency, and pressure were constant. Low-pressure points took up to 2 h; high-pressure points about 1 h each.

After finishing the low-temperature compression, the sample chamber was warmed up above the liquid-vapor critical temperature and the overpressure released until the sample chamber was at saturated vapor pressure. The sample was then cooled again, this time to a temperature slightly above the phase-separation temperature, and another compression took place. One could determine that the sample was indeed at saturated vapor pressure by noting that further filling took place before the pressure (as determined by the sample-chamber frequency) in the sample chamber started increasing.

B. Capacitor Model

The data were analyzed using the assumption that the density of the mixture is related to its dielectric constant by the Clausius-Mossotti relation

$$(\epsilon - 1)/(\epsilon + 2) = (\tfrac{4}{3}\pi)(p/v_m), \qquad (8)$$

and that the molar polarizability p is independent of pressure and temperature and is the same for He^3 and He^4.[20] Solving Eq. (8) and the parallel-resonant-circuit equation, one gets

$$v_m(s, P, T) = \frac{3\gamma v_0}{\omega_0^2/\omega^2 - 1} + v_0, \qquad (9)$$

where

$$v_0 = \tfrac{4}{3}\pi p = 0.5156\ \text{cm}^3; \quad \gamma = (1 + C_s/C_0)^{-1} C_s$$

is that portion of the capacitance that contains no liquid, and C_0 is that part that does contain liquid; ω_0 is the empty frequency, and ω is the frequency with the capacitor filled with mixture at pressure P, temperature T, and concentration x. The unknown constant $3\gamma v_0$ is determined at the beginning of each run by the frequency change on filling the capacitor and the values of $v_m(x, P, T)$ for P = saturated vapor pressure determined by Edwards *et al.*[7] For pure He^4, the saturated-vapor-pressure value of v_4 is that of Kerr and Taylor.[21] From one filling to the next, $3\gamma v$ always changed less than 0.1%.

There were two corrections to the raw-frequency data. One was an unexpected dependence on temperature. It became observable at 500 mK and increased linearly with inverse temperature to 300 Hz at 50 mK. The correction was obtained by recording the sample-chamber frequency as the cell was cooled while filled with a 0.1% mixture at saturated vapor pressure to provide thermal contact with the internal thermometers. A shift of 300 Hz corresponds, for instance, to approximately one-tenth of the total frequency change observed when the 10.0% mixture was cooled at saturated vapor pressure from 500–50 mK, so that ignoring this correction would lead to an error of 0.4% (absolute) in the concentration. It is believed to be due to the tank circuit coil located outside the sample chamber and thermally grounded to it. The coil was made by winding it on a Teflon rod and then coating it with Stycast 2850GT to give it rigidity. We think the frequency increase at low temperatures is probably due to the paramagnetic susceptibility of the Stycast. A rough calculation, assuming a reasonable filling factor for the coil and the data for Stycast given by Salinger and Wheatley,[22] gives the right order of magnitude for the shift.

Another correction needed to be made due to the pressure dependence of the capacitor. By compressing He gas at 77 K and using its known density, it was determined that any pressure corrections present were linear in P, but it was not possible to determine the magnitude in this way because of lack of knowledge of γ. Above 4 K, the characteristics of the tunnel diode change, and this changes the value of γ in an unknown way. The capacitor, being completely surrounded by fluid, however, should depend on pressure only through the compressibility of its construction material, copper. A calculation of this effect yielded a correction of only 17 Hz at 24 atm. This linear correction was used for all the data.

Drift in the sample-chamber oscillator was not a problem. It was observed to be stable to ±10 Hz over periods of 12–14 h.

IV. RESULTS AND DISCUSSION

A. He^4 Compression

Pure He^4 was compressed at two different times more than a month apart. The first compression was at 0.54 K and the second at 0.38 K. The molar volumes calculated from the first compression were consistently about 0.006 cm^3 larger than the second. The source of this systematic error may have been the pressure calibration. Our stated uncertainty in pressure (due mainly to drift in the transducer) gives rise to an uncertainty of about ±0.003 cm^3 in the molar volume. We have chosen the mean values of these two compressions for all our calculations and present smoothed values at $\frac{1}{2}$-atm intervals in Table I. The value for $P=0$ is that of Kerr and Taylor,[21] and was used for calibration of the capacitor as discussed in Sec. III.

The values of v_4 in Table I differ systematically from those of Boghosian and Meyer[1] at the higher pressures. (They also normalize their data at $P=0$ to the data of Kerr and Taylor.) At 20 atm, our molar volumes are 0.06 cm^3 larger than theirs. The most likely source of systematic difference between our data and theirs is an unaccounted pressure dependence in our capacitor. To force our data to agree with theirs, we would have to attribute a pressure dependence to our capacitor 35 times greater than calculated (about 600 Hz at 20 atm). We have not normalized our data to theirs because the uncertainty in their pressure correction is of the same order of magnitude as the necessary correction for our capacitor. Such a systematic error, however, would affect the values of α and x very little (see Secs. IV B and IV C.

We have differentiated the data in Table I to obtain isothermal compressibilities which are shown in Fig. 2 along with values of Boghosian and Meyer.[23] As a further check on the consistancy of our data, we have used these compressibilities to calculate first-sound velocities. Below 1.2 K, $k_t/k_S - 1 = \lesssim 10^{-4}$, so that little error is made by using the isothermal compressibility instead of the aidabatic value. In Fig. 3, we show s_4 calculated from

$$s_4^2 = v_4/m_4 k_t\,, \tag{10}$$

using both our data and that of Boghosian and Meyer.[1, 23] We also show the direct first-sound measurements of Atkins and Stasior.[24] As can be seen, the agreement with the latter is good.

B. High-Temperature Compression of Mixtures

We have compressed mixtures of molar concentration 6.41%, 8.27%, 9.18%, and 10.0% at temperatures ranging from 0.2–0.5 K. From these molar volumes, we have calculated the BBP parameter α from Eq. (3) in the form

$$\alpha(P,T) = [v_m(x,P,T)/v_4(P,T) - 1]/x\,. \tag{11}$$

As mentioned in Sec. III, we normalized the data by using the values for $v_m(x, 0, T)$ determined by Edwards *et al.*,[7] that is,

$$v_m(x,0,T) = v_4[1 + (0.284 - 0.032T)x]. \tag{12}$$

TABLE I. Smoothed values of He^4 molar volumes.

P (atm)	V_m (cm^3)	P (atm)	V_m (cm^3)
0	27.580	11.5	24.925
0.5	27.419	12.0	24.843
1.0	27.260	12.5	24.764
1.5	27.104	13.0	24.686
2.0	26.959	13.5	24.610
2.5	26.819	14.0	24.535
3.0	26.683	14.5	24.462
3.5	26.553	15.0	24.390
4.0	26.427	15.5	24.321
4.5	26.305	16.0	24.252
5.0	26.187	16.5	24.184
5.5	26.073	17.0	24.118
6.0	25.961	17.5	24.053
6.5	25.854	18.0	23.989
7.0	25.750	18.5	23.927
7.5	25.649	19.0	23.865
8.0	25.549	19.5	23.804
8.5	25.454	20.0	23.744
9.0	25.360	20.5	23.687
9.5	25.269	21.0	23.629
10.0	25.180	21.5	23.571
10.5	25.092	22.0	23.515
11.0	25.008	22.5	23.458

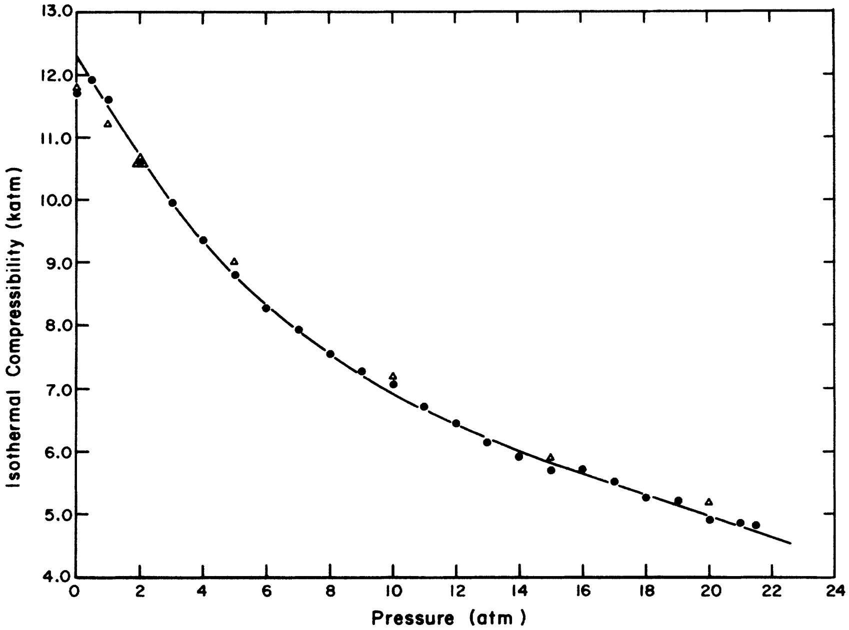

FIG. 2. Isothermal compressibility of He^4. This experiment ●; Boghosian and Meyer (Ref. 23) △.

The resulting values of $\alpha(P, T)$ for $T = 0$ are shown in Fig. 4. In reducing the data, we assumed α is independent of concentration in the range of this experiment. This has been shown to be a good assumption for $P = 0$ and concentrations up to 15%. We also assume that the temperature coefficient of α in (12) is independent of pressure. If this were not true for $P \neq 0$, one would expect to see systematic differences in the $\alpha(0)$-versus-P data. There is some scatter in Fig. 4 at intermediate pressures, but no outstanding systematic deviations. At high pressures the agreement is especially good. We must conclude then that, within the accuracy of these measurements, there is no concentration dependence in α and no pressure dependence in the temperature coefficient of α. The latter has been calculated using the Landau-Pomeranchuk model in Refs. 1 and 7, including interactions in Ref. 25. The resulting coefficient is

$$(R/v_4)\left(k(x) - \frac{3}{2}\frac{\partial \ln m_0^*}{\partial P}\right), \qquad (13)$$

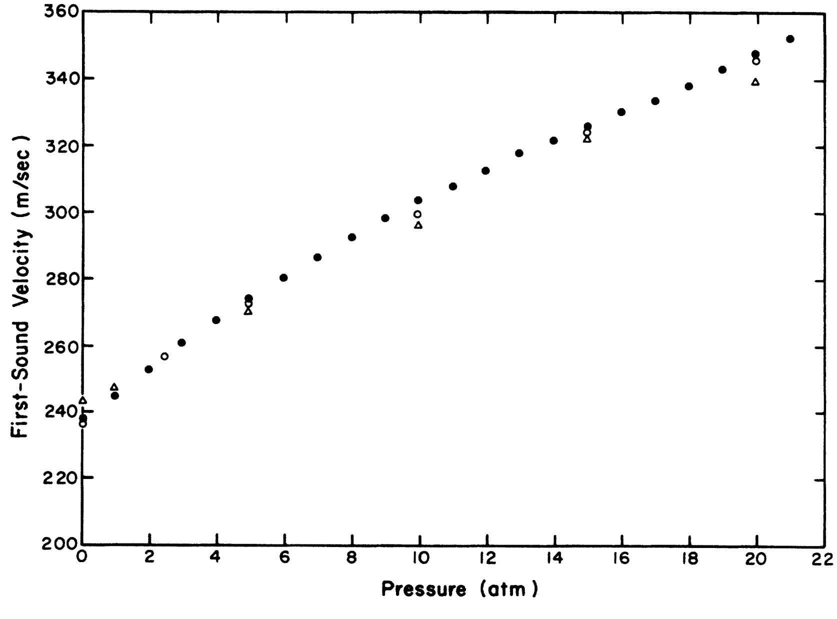

FIG. 3. First-sound velocity in He^4. This experiment ●; Boghosian and Meyer (Ref. 24) △; Atkins and Stasior (Ref. 24) ○.

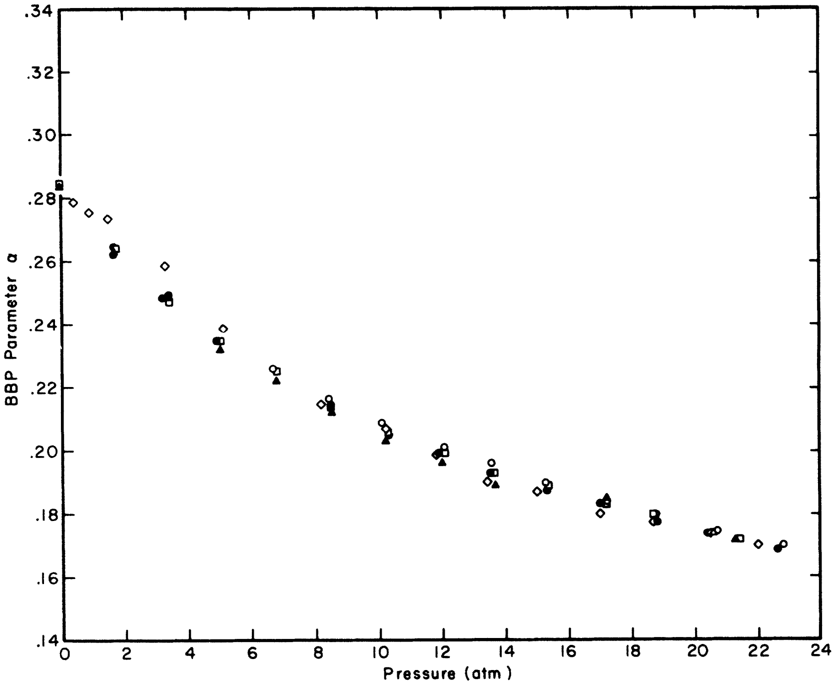

FIG. 4. The BBP parameter α extrapolated to $T=0$: 6.41% compressed at 0.2 K □; 6.41% compressed at 0.52 K△, 8.27% compressed at 0.33 K○; 9.18% compressed at 0.33 K○; 10.0% compressed at 0.32 K .

where $$k(x)=k_4-x\frac{\partial\alpha_0}{\partial P}\ ,$$

k_4 is the He^4 compressibility, and α_0 is the value of α at $T=0$. The value 0.032 K^{-2} for (13) leads to the value 0.0151 atm^{-1} for $\partial \ln m_0^*/\partial P$ at $P=0$.[7] This is in disagreement with the value 0.0108 atm^{-1} obtained from second-sound measurements.[26] Phase-separation measurements in Ref. 25 lead to the value 0.0138 atm^{-1}, which also does not agree with the second-sound measurements. If one, however, accepts the second-sound value at higher pressures, then (13) leads to a calculated value of the temperature coefficient of 0.030 K^{-2} at 20 atm and 0.026 K^{-2} at 10 atm which agrees within experimental error with our experiment.

As we mentioned in Sec. I, α has a very simple relationship to the properties of pure He^4, namely,

$$v_4\alpha=(\tfrac{1}{3})\left(\frac{\partial\langle \mathrm{KE}\rangle}{\partial P}\right)\ . \tag{14}$$

Equation (14) is probably correct to at least 1.0%.[11] From knowledge of α, therefore we gain knowledge that cannot easily be obtained from measurements on pure He^4.

Equation (14) can be integrated to give values of $\langle \mathrm{KE}\rangle$ relative to the value at $P=0$. Davison and Feenberg[11] have estimated $\langle \mathrm{KE}\rangle$ for $P=0$ to be 14.3 K. Their result is based on a calculation using Brillouin-Wigner perturbation theory. They find that

$$\langle \mathrm{KE}\rangle=3(L_{04}-E_{03}+\epsilon_2), \tag{15}$$

where L_{04} is the latent heat of pure He^4, and ϵ_2 is a second-order perturbation energy with value calculated by them to be 0.33 K. Figure 5 shows $\langle \mathrm{KE}\rangle$ computed from Eqs. (14) and (15) as a function of He^4 density. Integration of Eq. (15) tends to cancel out the large systematic differences between our α and that of Boghosian and Meyer. For comparison, we have included in Fig. 5 the results of some recent theoretical calculations for He^4.[13, 27] Figure 6 shows the values of $\langle \mathrm{PE}\rangle$, the ground-state potential energy for He^4. To obtain these numbers, we used our values for $\langle \mathrm{KE}\rangle$ and the total ground-state energies calculated from the thermodynamic relation

$$e_4=g_4-Pv_4=-L_{04}+\int_0^P v_4dP-Pv_4\ , \tag{16}$$

where e_4 and g_4 are the energy and Gibbs energy for He^4. Figures 5 and 6 would seem to indicate the calculations of $\langle \mathrm{KE}\rangle$ are quite good, whereas most of the approximately 1 K discrepancy between calculated and experimental ground-state energies can be attributed to $\langle \mathrm{PE}\rangle$. All of the theoretical calculations use the Lennard-Jones (6,12) potential with de Boer-Michel parameters chosen by fitting the experimental second virial coefficient for He to the theoretical value over a wide range of temperature. Massey,[28] on the other hand, has shown the experimental ground-

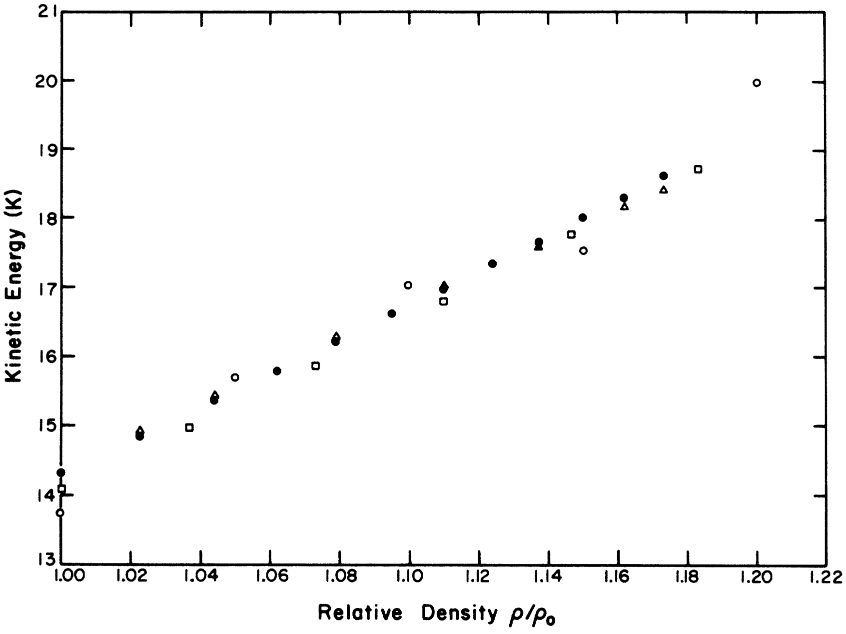

FIG. 5. Ground-state kinetic energy of pure He^4. This experiment ●; Boghosian and Meyer (Ref. 23) △; Massey and Woo (Ref. 12) □; Shiff and Verlet (Ref. 25) ○.

state energy can be obtained by shifting the minimum in the (6, 12) potential away from the de Boer-Michel value toward larger r by only 3 %. In his calculation, however, the ground-state energy deviates from the experimental one at high densities, whereas it can be seen in Figs. 5 and 6 that the calculation by Massey and Woo[13] using the de Boer-Michel values produces a density dependence that is very close to the experimental one. We should also note that classical calculations with the Lennard-Jones potential, with parameters determined from gaseous data, produce ground-state energies for such systems as liquid argon that agree very well with experiment over a wide range in density.

Figure 7 shows α, this time as a function of He^4 density, in order to compare our results with recent theoretical calculations by Massey and Woo,[13] and Davison and Feenberg.[12] Curve 3 of Davison and Feenberg is similar to that of Massey and Woo because they use the latter's ground-state results for pure He^4 along with the experimental velocity of sound. Curves 1 and 2 of Davison and Feenberg rely on the calculation of Massey.[28] The other cal-

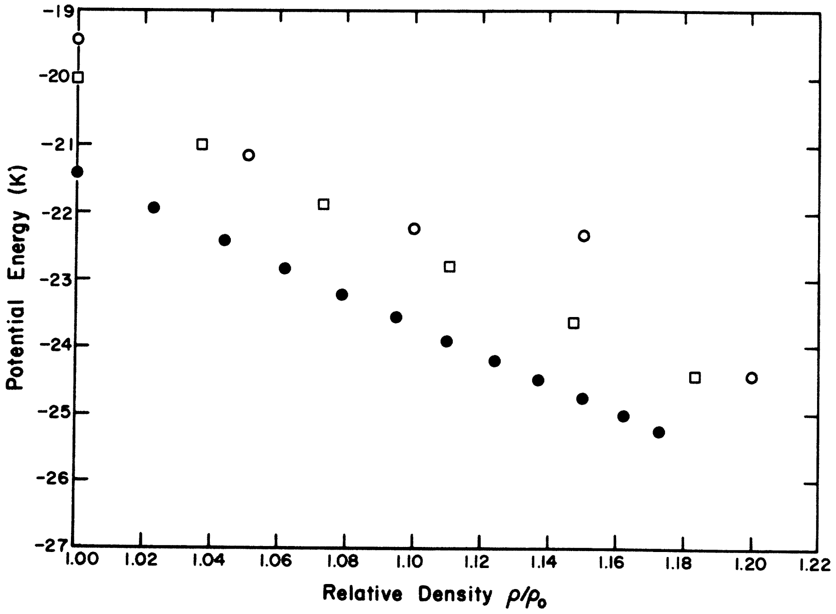

FIG. 6. Ground-state potential energy of pure He^4. This experiment ●; Massey and Woo (Ref. 12) □; Shiff and Verlet (Ref. 25) ○.

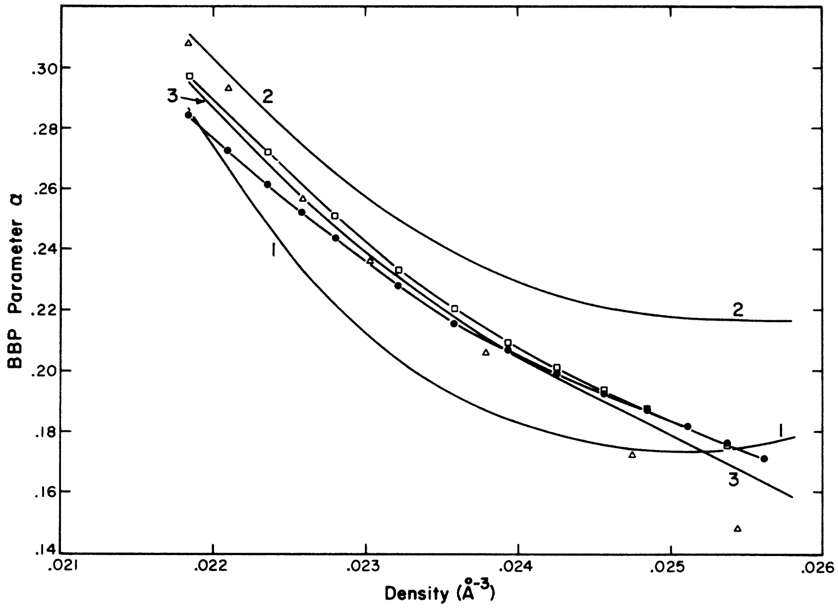

FIG. 7. BBP parameter α. This experiment ●; Massey and Woo (Ref. 12 using our v_4 and Eq. 14) □; Boghosian and Meyer (Ref. 1) △; Davison and Feenberg (Ref. 11) solid line (see text for explanation of curves numbered 1, –3).

culations use the de Boer-Michel parameters. Curve 1 makes use of theoretical velocities of sound, whereas in curve 2 experimental values have been used. All of the calculations make use of Eq. (14). One cannot calculate α from the data of Shiff and Verlet because of the large fluctuations evident in Figs. 5 and 6.

We cannot explain the disagreement shown in Fig. 7 between our data and that of Boghosian and Meyer. Several independent experiments have measured α to be near 0.28, so this value is probably quite good.[7,25,29] If Boghosian and Meyer's α's are all shifted down to produce agreement at $P = 0$, then the cancelation in the calculation of $\langle \mathrm{KE} \rangle$ will be removed, and systematically lower values will result.

We should point out that an unaccounted for linear pressure dependence in the measuring capacitor C_0 cancels out in first order in the calculation of α, because it enters both v_4 and v_m. A pressure dependence of 1000 Hz in ω_0 at 20 atm, for instance, would lead to an error of only 0.5% in the value of α. This is smaller than our estimated ±0.002 error in α.

C. Low-Temperature Compression

For two samples, the 8.27 and 10.0%, the molar volumes were measured from above the phase-separation temperature to 50 mK. From these molar volumes and Eq. (3) in the form

$$x = (v_m / v_4 - 1)/\alpha \, , \qquad (17)$$

and using $\alpha(T)$ from Edwards *et al.*,[7] one can calculate the concentration in the lower phase as a function of temperature. We then fit the resulting data below 150 mK to an equation of the form

$$x = x_0 (1 + \beta T^2) \, , \qquad (18)$$

in order to compare our results with other experimenters. The results are shown in Table II. These values are in good agreement with Edwards *et al.*[7] The dielectric method for measuring densities was also used by Edwards, *et al.*[7] and Abraham *et al.*[25] Shermer, Passell, and Rorer[8] use neutron scattering to measure the He^3 number density of both phases.

The results of the compressions at 50 mK are shown in Fig. 8. The concentrations were found by again using Eq. (17), this time with our values of α(50 mK, P). Compressions were performed on 8.27, 9.18, and 10.0% mixtures.

The compression of the 10.0% mixture shows the complete solubility curve and is believed to be accurate to ±0.10% (absolute). The 8.27 and 9.18% samples were compressed in order to establish absolute points on the curve that were independent of any calculated molar volumes. These mixtures are phase separated at the beginning of the compression. The 8.27% sample re-

TABLE II. Phase separation at saturated vapor pressure.

	X_0(%)	β(K^{-2})
8.27%	6.46 ± 0.08	9.85
10.0%	6.46 ± 0.08	9.97
Edwards *et al.*	6.40 ± 0.07	10.8
Schermer *et al.*	6.84 ± 0.06	11.1 ± 0.7
Abraham *et al.*	6.66 ± 0.06	9.3

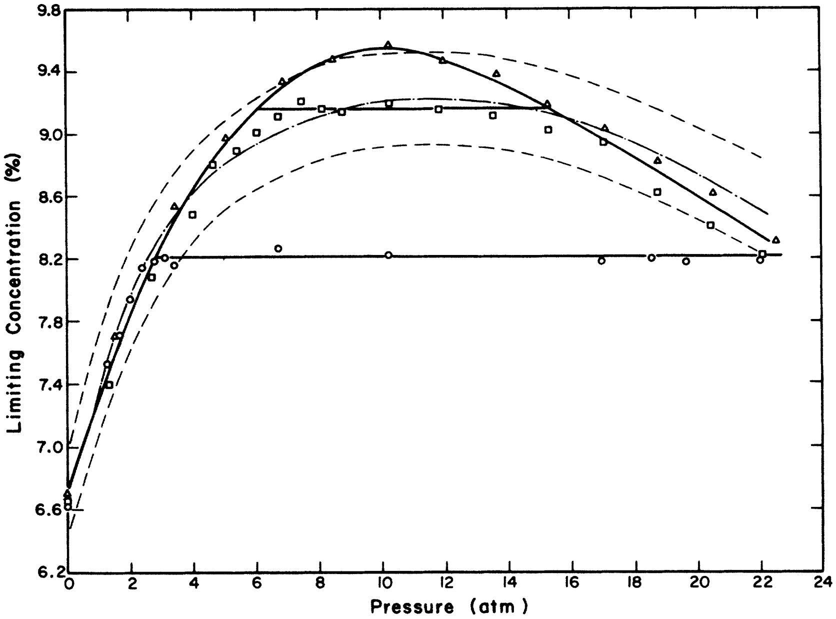

FIG. 8. Limiting concentration of He^3 in He^4 at $T=50$ mK. 8.27% ○; 9.18% □; 10.0% △; calculated with Ebner potential dot-dashed line.

mixes at about 3 atm; the 9.18% at about 7 atm. The 9.18% data were not taken at complete equilibrium and are probably uncertain to ±0.2% (absolute). We have included this data because it was not clear whether, once remixed, it would again phase separate. Edwards has pointed out that one might expect mixtures not under their saturated vapor pressure to supercool.[30] In earlier versions of this experiment we have observed supercooling of up to 45 mK at pressures of a few atmospheres. One might expect the analogous effect in these compressions, i.e., supersaturation. Figure 8 indicates, however, that the 9.18% sample does phase separate again at the higher pressures. With greater pressure and concentration resolution, however, one might see supersaturation.

As can be seen, the limiting solubility rises rapidly at first, reaching a maximum of about 9.5% at 10 atm; then drops off to about 8.3% at 22 atm. This behavior differs from that predicted by the model calculation of van Leeuwen, and Cohen,[31] based on a mixture of hard-sphere fermions and bosons.[32] Their calculations is an extension of earlier calculations by Cohen and van Leeuwen[33] that predicted incomplete phase seperation at $T=0$ for the superfluid phase. The calculation produces a phase diagram that qualitatively resembles the experimental result in a tantalizing manner. The λ line meets the phase separation at its peak,[34] the upper phase becomes pure He^3 at $T=0$,[35] and the lower phase becomes a 20% mixture of He^3 in He^4.

The most interesting part of their calculation, however, is that the whole phase-separation phenomena is intimately dependent on the difference in statistics of the two components, whereas the mass difference is less important.

On the other hand, if the behavior in Fig. 8 is to be understood in terms of the empirical interaction approach of BBP, using the effective potential suggested by Ebner,[14] then the mass difference of the atoms is primarily responsible for phase separation; the statistics playing a nonexplicit role. This will be evident in the discussion below.

The concentration of He^3 in the lower phase can be calculated at $T=0$ by equating the chemical potential for He^3 in the upper phase to that for the He^3 in the lower phase. The resulting equation can then be solved for x.

For the lower phase, we use Eq. (6) with Ebner's potential, but modified for $P\neq 0$ as indicated in the Appendix. This potential was designed to empirically fit the spin-diffusion data in mixtures in the temperature range up to 1 K. It is known that it is in good agreement with the phase-separation data at saturated vapor pressure up to a concentration of about 15%.[7] Equating the two chemical potentials and solving for x, one obtains

$$x=x_0\,\frac{v_m(x,P,0)}{v_m(x_0,0,0)}\left(\frac{m_0^*(P)(T_0+T_P+xyT_B)}{m_0^*T_{f0}}\right)^{2/3}, \qquad (19)$$

where

$$y(x)=1-\frac{3}{4p_f^{\,3}}\int_0^{2p_f}q^2\left(1-\frac{q}{2p_f}\right)\frac{V_q}{V_0}\,dq\ ,$$

$$T_0=(E_{03}-L_{03})/R\ ,$$

$$T_p=\frac{1}{R}\int_0^p[v_3-(1+\alpha)v_4]\,dP\ ,$$

$$T_B = \alpha^2 m_4 s_4{}^2/R \quad ,$$

$$T_{f0} = T_f(P=0) \quad ,$$

and x_0 is the concentration for $P=0$. This equation must be solved recursively. As can be seen, some independent experimental information must also be used. We have used the He^3 molar-volume data of Boghosian, Meyer, and Rives,[36] the effective mass under pressure data of McClintock, Mueller, Guyer, and Fairbank,[26] and our values of v_m, s_4, α, and v_4. This calculation gives $x(P)$ at $T=0$. At 50 mK, all of the concentrations will be slightly higher. Ebner[14] has also calculated the chemical potential at finite temperature. Using his expression and the entropy for pure He^3 tabulated by Radebaugh,[37] we can calculate β in Eq. (18).[15] Thus, the values obtained from Eq. (19) can be corrected for temperature. This has been done and is shown as the dot-dash line in Fig. 8. Ebner states that his potential is probably not accurate to more than 15%. The dashed lines in Fig. 8 show this uncertainty in V_q.

Figure 8 can be most easily understood by considering the expression dx/dP. We start by differentiating the equation

$$\mu_3{}^0 = \mu_3[x(P), P] \tag{20}$$

to get

$$\frac{dx}{dP} = [v_3 - (1+\alpha)v_4] \Big/ \left(\frac{\partial \mu_3}{\partial x}\right)_P \quad , \tag{21}$$

where we have again used the result in the Appendix. The derivative in the denominator is easily evaluated from Eq. (6). The result to lowest order in the small quantity αx,

$$\frac{dx}{dP} = \frac{3}{2}\,\frac{x[v_3 - (1+\alpha)v_4]}{k_B T_f\{1 - \frac{3}{2}[x\alpha^2 m_4 s_4{}^2(1+1/2F)]/k_B T_f\}} \; , \tag{22}$$

where F is the exchange integral defined by Ebner,[14] which depends only weakly on x.

The denominator of (22) remains positive up to 22 atm, hence we see that the main features of Fig. 8 arise due to the term $v_3 - (1+\alpha)v_4$. This term is positive up to 10 atm, where it crosses zero, becomes negative, and is fairly constant above 15 atm. Since

$$+L_{03} - \int_0^P v_3\,dP$$

is the binding energy per mole in He^3,

and $$+E_{03} - \int_0^P (1+\alpha)v_4\,dP$$

is the binding energy per mole for He^3 atoms in the mixture (for $x \to 0$), it is clear why their difference dominates the behavior of the solubility.

The lack of detailed agreement between experiment and this calculation cannot as yet be attributed to Ebner's interaction potential, because of the uncertainty in the term

$$\int_0^P [v_3 - (1+\alpha)v_4]\,dp.$$

The He^3 molar volumes used here were measured relative to values at 1.2 K, which had been measured by a non-dielectric method.[38] The values at 1.2 K are accurate to only 0.1%. This leads to an estimated uncertainty in

$$\int_0^P [v_3 - (1+\alpha)v_4]\,dp$$

of about 10%, which gives rise to a possible error of ±0.2% (absolute) in x at the higher pressures. Hence, at the moment, we can only say that Ebner's potential is consistent with our results.

Our experimental values of $x(P)$ at 1-atm intervals are listed in Table III.

Note added in proof. The results presented in Fig. 8 are in excellent agreement with the recently published solubility limits obtained in osmotic-pressure measurements by J. Landau, J. T. Tough, N. R. Brubaker, and D. O. Edwards, Phys. Rev. Letters 23, 284 (1969).

ACKNOWLEDGMENTS

The authors wish to acknowledge the constant interest and stimulation of Dr. D. M. Lee, whose group initiated work at this laboratory on He^3-He^4 mixtures. Also they would like to thank their colleagues E. Smith and A. Greenberg for experimental help during the early part of this work, and W. Schwenterly who built the final cryostat and assisted in the final stages of the experiment. One

TABLE III. Limiting concentration at $T=50$ mK (±0.1%).

P(atm)	X(%)	P	X
0	6.65	12	9.45
1	7.30	13	9.40
2	7.85	14	9.30
3	8.30	15	9.20
4	8.65	16	9.08
5	8.92	17	8.96
6	9.15	18	8.85
7	9.30	19	8.72
8	9.44	20	8.60
9	9.50	21	8.48
10	9.54	22	8.35
11	9.52	•••	•••

of us (RCR) would like to acknowledge conversations with Dr. D. O. Edwards (Ohio State University). Finally, they wish to thank Dr. G. Chester for suggesting corrections in the initial manuscript.

APPENDIX

A. Change in μ_3 with P

The Gibbs-Duhem relation for constant T is

$$N_3 d\mu_3 + N_4 d\mu_4 = V dP. \tag{A1}$$

Thus, the change in μ_3 at constant N_3 and N_4 is

$$N_3\left(\frac{\partial\mu_3}{\partial P}\right)_{N_3, N_4, T} = V - N_4\left(\frac{\partial\mu_4}{\partial P}\right)_{N_3, N_4, T}. \tag{A2}$$

Now Eq. (3) from the text can be written

$$V = v_4[N_4 + (1+\alpha)N_3].$$

This equation along with the Maxwell relation,

$$\left(\frac{\partial\mu_4}{\partial P}\right)_{N_3, N_4, T} = \left(\frac{\partial V}{\partial N_4}\right)_{N_3, P, T}$$

can be used to show that

$$\left(\frac{\partial\mu_4}{\partial P}\right)_{N_3, N_4, T} = v_4.$$

Thus, $$\left(\frac{\partial\mu_3}{\partial P}\right)_{N_3, N_4, T} = (1+\alpha)v_4 \quad ,$$

or

$$\mu_3(N_3, N_4, P, T) = \mu_3(N_3, N_4, 0, T) + \int_0^P (1+\alpha)v_4 dP.$$

B. $\mu_3{}^0$ at Finite T

For pure He^3 we may integrate the Gibbs-Duhem relation directly to get

$$\mu_3{}^0(P, T) = -L_{03} + \int_0^P v_3(P, 0)dP - \int_0^T s_3(P, T)dT.$$

In the temperature range of this experiment, the entropy of compression, $s_3(P, T) - s_3(0, T)$, can be ignored, thus

$$\mu_3{}^0(P, T) = -L_{03} + \int_0^P v_3(P, 0)dP - \int_0^T s_3(0, T)dT.$$

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*Work supported by the National Science Foundation under Contract No. GP-10698 and the Advanced Research Projects Agency through the Materials Science Center at Cornell University, MSC Report No. 1184.

†This paper is based on a thesis submitted to Cornell University by G. E. Watson in partial fulfillment of the requirements for the Ph. D. degree. Present address: Physics Department, American University of Beirut, Beirut, Lebanon.

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PHYSICAL REVIEW VOLUME 188, NUMBER 1 5 DECEMBER 1969

Paired-Phonon Analysis for the Ground State and Low Excited States of Liquid Helium†

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(Received 1 July 1969)

The paired-phonon analysis operates in the function space generated by product functions compounded from (i) a starting trial function ψ of the Bijl-Dingle-Jastrow-type (BDJ) (a product of two-particle correlation factors $\exp[\frac{1}{2}U(r_{ij})]$; (ii) paired-phonon factors $\rho_{\vec{k}}\rho_{-\vec{k}}$ to all powers, (iii) multiple phonon factors $\rho_{\vec{k}}\cdots\rho_{\vec{l}}$ to all powers, with neglect of all matrix elements representing processes in which phonons coalesce, split, or scatter. Results in the present study include (i) a simpler and more general derivation of the fundamental relations; (ii) proof that the improved ground-state trial function $\hat{\psi}$ generated by the analysis is still in the BDJ function space [with $U(r)$ replaced by $U(r)+\delta U(r)$]; (iii) a formula expressing $\delta U(r)$ in terms of $S(k)$, the starting liquid-structure function, and $w(k)$, the residual interaction function; (iv) a convenient representation of the phonon factor $\rho_{\vec{k}}$ as a linear combination of phonon creation and annihilation operators; (v) explicit statement of the relation between the optimization condition $w(k)\equiv 0$ and the variational extremum property of the expectation value of H in the BDJ-type function space; (vi) usable approximate procedures for evaluating the residual interaction function $w(k)$ based on the hypernetted-chain (HNC) and Percus-Yevick (PY) relations; and (vii) numerical evaluation of $w(k)$, the energy shift δE, and the improved liquid-structure function $\hat{S}(k)$ using ψ's computed by Massey and Woo as starting functions. For ^{4}He at the equilibrium density, $(1/N)\delta E \sim -0.7\,^\circ\mathrm{K}$; for the hypothetical boson-type ^{3}He system at $\rho=0.0164\,\mathrm{Å}^{-3}$, $(1/N)\delta E \sim -0.3\,^\circ\mathrm{K}$ (HNC) or $-0.5\,^\circ\mathrm{K}$ (PY). In the discussion, emphasis is placed on the practical possibility of accurate numerical evaluation of the interaction function $\omega(k)$ by the method of molecular dynamics applied to systems containing 10^2-10^3 particles.

I. INTRODUCTION

Recent theoretical studies [1-5] of the ground state of liquid ^{4}He are based on the use of a Bijl-Dingle-Jastrow-type (BDJ) trial function in evaluating the expectation value of the Hamiltonian operator:

$$|0\rangle \equiv \Psi(1,2,\ldots,N) = \prod_{1\leq i\leq j\leq N} e^{U(r_{ij})/2} \Big/ \Big(\int \Pi e^{U} d\vec{r}_{1,2,\ldots,N}\Big), \tag{1}$$