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Theory of Binary Boson Solutions[†]

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The properties of a dilute solution of mass-

3 bosons in liquid He⁴ at low temperatures are computed via a variational procedure. A set of coupled integro-differential equations is solved yielding the ground state energy per particle, the binding energy of He³ in He⁴, the volume excess parameter α , the (3,3), (4,3) and (4,4) distribution functions, and the long wave-length limit of the effective interaction between He³ quasi-particles in He⁴. Results compare favorably with experiment and with phenomenological theories.

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I. Introduction

The properties of dilute solutions of He^3 in liquid He^4 have received considerable attention, both theoretically and experimentally, over the past several years. Bardeen, Baym and Pines^{1,2} and separately, Emery,³ proposed a phenomenological theory which assumes a quasiparticle Hamiltonian at the outset, and uses experimental data to fit certain undetermined parameters. The pertinent physical parameters in such a theory include the binding energy of one He^3 atom in liquid He^4 , the effective mass of a He^3 quasiparticle, and the effective interaction between a pair of He^3 quasiparticles. We, on the other hand, entertained the goal of achieving a completely microscopic theory of He^3 - He^4 solutions. In two recent papers,^{4,5} we reported on a calculation which starts from the Hamiltonian describing bare helium atoms, and derives a quasiparticle Hamiltonian containing no free parameters and yielding numerical results which can be compared directly with experiment.

We consider in this paper a binary solution of mass-3 and mass-4 bosons. Such a system serves as a first approximation to the realistic He^3 - He^4 solution. An understanding of the properties of this system yields information about the properties of the He^3 - He^4 solution which depend primarily on the mass difference and which are relatively uninfluenced by the Fermion nature of the He^3 atoms. These properties include the binding energy of one He^3 in liquid He^4 , the long-wavelength (or static) limit of the effective quasiparticle interaction, and the spatial distribution of the He^3 atoms in the solution. Furthermore, the results of this calculation form important input information to the complete theory of dilute He^3 - He^4 solutions mentioned above.^{4,5}

In section II we define the problem of a binary boson solution and formulate a procedure to solve for its ground state. The actual computation is described in section III (and the Appendix), leading to numerical results reported and compared with experiment in section IV. In section V we discuss the limitations of the theory and suggest possible improvements.

II. The Binary Boson Solution

The binary boson solution is defined by the Hamiltonian

$$H = \frac{-\hbar^2}{2m_4} \sum_{i=1}^{N_4} \nabla_i^2 + \frac{-\hbar^2}{2m_3} \sum_{k=N_4+1}^N \nabla_k^2 + \sum_{i < k=1}^N v(r_{ik}). \quad (1)$$

m_4 and m_3 are respectively the masses of two types of particles with Bose statistics. Coordinates 1 through N_4 refer to the mass-4 bosons, the rest to mass-3 bosons. $v(r)$ is a two-particle potential, which is strongly repulsive at short range and may be taken to be of the form

$$v(r) = 4\epsilon \left\{ \left(\frac{a}{r} \right)^{12} - \left(\frac{a}{r} \right)^6 \right\}. \quad (2)$$

We assume here that the mass-4 and mass-3 bosons interact through the same potential, even though this fact does not result in any simplification of the calculation. This assumption is consistent with our present knowledge of the interactions between He^3 and He^4 atoms. However the theory to be discussed here is equally applicable to systems in which the particles interact through different potentials.

The concentration (of mass-3 bosons), particle densities and total volume are denoted respectively by $x \equiv N_3/N$, $\rho_3 = N_3/\Omega = (N-N_4/\Omega)$,

$\rho_4 = N_4/\Omega$, and Ω ; and we operate in the limit $N_3 \rightarrow \infty$, $N_4 \rightarrow \infty$, and $\Omega \rightarrow \infty$ such that $\rho_3 = \text{constant}$, $\rho_4 = \text{constant}$, and $\rho \equiv \rho_3 + \rho_4 = \text{constant}$. We seek an approximate ground state eigenfunction of the Hamiltonian in Eq. (1).

The ground state properties of pure liquid He^4 are known to be described fairly accurately by the Jastrow wavefunction^{6,7}

$$\psi(1,2,\dots,N) = \prod_{i<j=1}^N e^{\frac{1}{2}u(r_{ij})} \quad (3)$$

This suggests that a generalized form of the Jastrow wavefunction might be appropriate for the ground state of a binary boson solution. We thus choose as a trial wavefunction

$$\begin{aligned} \psi_0(1,2,\dots,N_4; N_4+1,\dots,N) \\ = \prod_{i<j=1}^{N_4} e^{\frac{1}{2}u^{(4,4)}(r_{ij})} \prod_{i=1}^{N_4} \prod_{k=N_4+1}^N e^{\frac{1}{2}u^{(4,3)}(r_{ik})} \prod_{k<\ell=N_4+1}^N e^{\frac{1}{2}u^{(3,3)}(r_{k\ell})}. \end{aligned} \quad (4)$$

$u^{(4,4)}(r)$, $u^{(4,3)}(r)$ and $u^{(3,3)}(r)$ are functions describing the correlations between (4,4), (4,3) and (3,3) particle-pairs, respectively. These "correlating functions" satisfy the usual boundary conditions

$$\begin{aligned} \lim_{r \rightarrow 0} u^{(\alpha,\beta)}(r) &= -\infty \\ \lim_{r \rightarrow \infty} u^{(\alpha,\beta)}(r) &= 0 \\ \alpha, \beta &= 4, 3 \end{aligned} \quad (5)$$

In terms of the wavefunction ψ_0 , three types of pair distribution functions can be defined as follows:

$$\rho_{\alpha} \rho_{\beta} g^{(\alpha, \beta)}(r_{i_{\alpha} i_{\beta}}) = N_{\alpha} (N_{\beta} - \delta_{\alpha\beta}) \int |\psi_0|^2 dr_{\sim(i_{\alpha}, i_{\beta})} I, \quad (6)$$

where $dr_{\sim(i_{\alpha}, i_{\beta})}$ denotes $dr_{\sim 1} dr_{\sim 2} \dots dr_{\sim N}$ with $dr_{\sim i_{\alpha}}$ and $dr_{\sim i_{\beta}}$ omitted. Again α and β can be 4 or 3, and $I = \int |\psi_0|^2 dr_{\sim 1} dr_{\sim 2} \dots dr_{\sim N}$. $g^{(\alpha, \beta)}(r_{i_{\alpha} i_{\beta}})$ is the probability (relative to a random distribution) that, given a particle of type α at the origin, a particle of type β will be found at a distance $r_{i_{\alpha} i_{\beta}}$ away.

We shall also need the three-particle distribution functions defined by

$$\rho_{\alpha}^3 g^{(\alpha, \alpha, \alpha)}(i_{\alpha}, j_{\alpha}, k_{\alpha}) = N_{\alpha} (N_{\alpha} - 1) (N_{\alpha} - 2) \int |\psi_0|^2 dr_{\sim(i_{\alpha}, j_{\alpha}, k_{\alpha})} / I, \quad (7)$$

$$\rho_{\alpha}^2 \rho_{\beta} g^{(\alpha, \alpha, \beta)}(i_{\alpha}, j_{\alpha}, k_{\beta}) = N_{\alpha} (N_{\alpha} - 1) N_{\beta} \int |\psi_0|^2 dr_{\sim(i_{\alpha}, j_{\alpha}, k_{\beta})} / I.$$

It is implied in the definitions, Eqs. (6)-(7) that these distribution functions are unaffected by a permutation of their superscripts and arguments.

The pair distribution functions must have the usual physical properties:

- (i) $g^{(\alpha, \beta)}(r)$ is a purely radial function;
- (ii) $\lim_{r \rightarrow \infty} [g^{(\alpha, \beta)}(r) - 1] = 0$;
- (iii) $g^{(\alpha, \beta)}(r)$ satisfies the normalization condition

$$\rho_{\alpha} \int [g^{(\alpha, \beta)}(r) - 1] + \delta_{\alpha\beta} = 0. \quad (8)$$

The importance of taking into account the difference in correlations between (4,4), (4,3) and (3,3) pairs is clear. Because of the lighter mass, a mass-3 particle has a larger zero-point energy and therefore occupies a larger specific volume than a mass-4 particle. A measure

of this increased volume is the parameter α , defined as the fractional increase in the volume of the system when a mass-4 particle⁸ is replaced by a mass-3 particle. Measurements on He³-He⁴ solutions give $\alpha \approx 0.3$ at zero pressure. Since a measure of the effective volume occupied by a particle is given approximately by the position of the first maximum in the pair distribution function, and for pure liquid He⁴, the maximum of $g^{(4,4)}(r)$ occurs at $r_0 = 3.4\text{\AA}$, we expect $g^{(4,3)}(r)$ to exhibit a maximum at $(1 + \alpha)^{1/3} r_0 \approx 3.7\text{\AA}$. Hence, $g^{(4,4)}(r)$ and $g^{(4,3)}(r)$ are expected to be quite different. The same is true for $g^{(3,3)}(r)$. These differences are allowed for in our present choice of the trial wavefunction.

In terms of $g^{(\alpha,\beta)}(r)$ and $u^{(\alpha,\beta)}(r)$, the expectation value of the Hamiltonian can now be expressed as follows

$$\langle H \rangle = \langle T \rangle + \langle V \rangle, \quad (9)$$

where

$$\begin{aligned} \langle T \rangle = & \frac{\hbar^2 \rho_4}{8m_4} [N_4 \int \nabla u^{(4,4)}(r) \cdot \nabla g^{(4,4)}(r) d\mathbf{r} \\ & + N_3 \int \nabla u^{(4,3)}(r) \cdot \nabla g^{(4,3)}(r) d\mathbf{r}] \\ & + \frac{\hbar^2 \rho_3}{8m_3} [N_4 \int \nabla u^{(4,3)}(r) \cdot \nabla g^{(4,3)}(r) d\mathbf{r} \\ & + N_3 \int \nabla u^{(3,3)}(r) \cdot \nabla g^{(3,3)}(r) d\mathbf{r}], \quad (10) \end{aligned}$$

and

$$\begin{aligned} \langle V \rangle = & N_4 \frac{\rho_4}{2} \int v(r) g^{(4,4)}(r) d\mathbf{r} \\ & + N_3 \rho_4 \int v(r) g^{(4,3)}(r) d\mathbf{r} \\ & + N_3 \frac{\rho_3}{2} \int v(r) g^{(3,3)}(r) d\mathbf{r}. \quad (11) \end{aligned}$$

If the $g^{(\alpha,\beta)}$'s are known, $\langle V \rangle$ can be computed immediately; for computing $\langle T \rangle$, however, the correlating function $u^{(\alpha,\beta)}$ must also be known.

Equations relating the correlating functions to the distribution functions are derived by applying appropriate differentiation operators to the definitions of the latter,⁶ Eq. (6). We obtain the following

$$\begin{aligned} \nabla_{12} g^{(4,4)}(r_{12}) &= g^{(4,4)}(r_{12}) \nabla_{12} u^{(4,4)}(r_{12}) \\ &+ \rho_4 \int g^{(4,4,4)}(1,2,3) \nabla_{13} u^{(4,4)}(r_{13}) dr_3 + \rho_3 \int g^{(4,4,3)}(1,2,N) \nabla_{1N} u^{(4,3)}(r_{1N}) dr_N, \end{aligned} \quad (12)$$

$$\begin{aligned} \nabla_{1N} g^{(4,3)}(r_{1N}) &= g^{(4,3)}(r_{1N}) \nabla_{1N} u^{(4,3)}(r_{1N}) \\ &+ \rho_4 \int g^{(4,4,3)}(1,2,N) \nabla_{2N} u^{(4,3)}(r_{2N}) dr_2 + \rho_3 \int g^{(4,3,3)}(1,N-1,N) \nabla_{N-1,N} u^{(3,3)}(r_{N-1,N}) dr_{N-1}, \end{aligned} \quad (13)$$

and

$$\begin{aligned} \nabla_{N-1,N} g^{(3,3)}(r_{N-1,N}) &= g^{(3,3)}(r_{N-1,N}) \nabla_{N-1,N} u^{(3,3)}(r_{N-1,N}) \\ &+ \rho_4 \int g^{(4,3,3)}(1,N-1,N) \nabla_{1N} u^{(4,3)}(r_{1N}) dr_1 + \rho_3 \int g^{(3,3,3)}(N-2,N-1,N) \nabla_{N-2,N} u^{(3,3)}(r_{N-2,N}) dr_{N-2}. \end{aligned} \quad (14)$$

These equations are obvious extensions of the BBGKY equation for a one-component fluid. The analogues for classical liquids have been used by Alder and others.⁹ As they stand, the equations are exact, albeit insoluble. They may be reduced to a tractable form by introducing the generalized superposition approximation (SA):

$$g^{(\alpha,\beta,\gamma)}(i_\alpha, i_\beta, i_\gamma) \approx g^{(\alpha,\beta)}(r_{i_\alpha i_\beta}) g^{(\beta,\gamma)}(r_{i_\beta i_\gamma}) g^{(\gamma,\alpha)}(r_{i_\gamma i_\alpha}). \quad (15)$$

We have employed approximations of this type in previous work concerning pure helium liquids, and have accumulated a certain amount of experience in estimating the degree of error committed. (See section V.) Alternate procedures of obtaining corresponding $u^{(\alpha,\beta)}_s$ and $g^{(\alpha,\beta)}_s$, which avoid the use of the SA, are available. In particular the distribution functions may be computed directly from their definitions by Monte Carlo integration techniques or molecular dynamics. However, the computer time needed for such calculations is much greater than an approximate solution of the generalized BBGKY equations; it is not obvious that the extra time required is rewarded by increased accuracy.¹⁰ (For a detailed comparison of Monte Carlo, molecular dynamics, and SA procedures, see references 5.)

III. Variational Calculation for the Ground State

Following earlier work,⁶ we parameterize analytic forms for $g^{(\alpha,\beta)}(r)$'s and calculate the corresponding $u^{(\alpha,\beta)}(r)$'s through Eqs. (12)-(14). The expectation value of H is then minimized with respect to variation of the parameters in $g^{(\alpha,\beta)}(r)$, thus selecting out an optimum set of pair distribution functions along with the corresponding wavefunction.

As a practical method of solving Eqs. (12)-(14) and from the point of view of obtaining the maximum physical understanding, we carry out the variational calculation via a three step procedure.

- (i) Consider a system of pure He^4 and a trial wavefunction of the form in Eq. (3). Determine $g^{(4,4)}(r)$ and $u^{(4,4)}(r)$ variationally.
- (ii) Replace a He^4 atom, say the N^{th} one, by a mass-3 boson, and introduce the trial wavefunction

$$\psi_0(1,2,\dots,N-1;N) = \prod_{i < j=i}^{N-1} e^{-\frac{1}{2}u^{(4,4)}(r_{ij})} \prod_{i=1}^{N-1} e^{-\frac{1}{2}u^{(4,3)}(r_{iN})}. \quad (16)$$

The energy expression now contains $g^{(4,4)}(r)$, $g^{(4,3)}(r)$, $u^{(4,4)}(r)$ and $u^{(4,3)}(r)$. Assuming that $g^{(4,4)}(r)$

has been optimally determined in step (i), we determine $g^{(4,3)}(r)$ variationally, solving in the process coupled equations for a new $u^{(4,4)}(r)$ and the $u^{(4,3)}(r)$.

- (iii) Replace N_3 He^4 atoms by the same number of mass-3 bosons and introduce the trial wavefunction of Eq. (4). Assuming that $g^{(4,4)}(r)$ and $g^{(4,3)}(r)$ have been fixed in step (ii), we finally determine $g^{(3,3)}(r)$ and an upper bound to the ground state energy of the binary boson solution, solving in the process coupled equations for new $u^{(4,4)}(r)$, new $u^{(4,3)}(r)$ and the $u^{(3,3)}(r)$.

Pure Liquid He^4

Step (i) has been carried out in a previous calculation.⁶ We shall use here the results of that calculation.

One Mass-3 Boson in Liquid He^4

In this case the coupled equations reduce to

$$\begin{aligned} \nabla_{12}^2 g^{(4,4)}(r_{12}) &= g^{(4,4)}(r_{12}) \nabla_{12}^2 u^{(4,4)}(r_{12}) \\ &+ \rho_4 \int g^{(4,4,4)}(1,2,3) \nabla_{13}^2 u^{(4,4)}(r_{13}) dr_3 + \rho_3 \int g^{(4,4,3)}(1,2,N) \nabla_{1N}^2 u^{(4,3)}(r_{1N}) dr_N, \end{aligned} \quad (17)$$

and

$$\begin{aligned} \nabla_{1N} g^{(4,3)}(r_{1N}) &= g^{(4,3)}(r_{1N}) \nabla_{1N} u^{(4,3)}(r_{1N}) \\ &+ \rho_4 \int g^{(4,4,3)}(1,2,N) \nabla_{2N} u^{(4,3)}(r_{2N}) d\tilde{r}_2. \end{aligned} \quad (18)$$

The solution of Eq. (18) is straightforward. The solutions of Eq. (17) requires the knowledge of $u^{(4,3)}(r)$, and a starting point: $u_{(0)}^{(4,4)}(r)$, for an iterative procedure. The former is provided by the solution of Eq. (18), and the latter is chosen such that

$$u_{(0)}^{(4,4)}(r) = u_p(r), \quad (19)$$

where $u_p(r)$ is the correlating function for pure liquid He^4 at the partial density ρ_4 , satisfying the equation

$$\nabla_{12} g^{(4,4)}(r_{12}) = g^{(4,4)}(r_{12}) \nabla_{12} u_p(r_{12}) + \rho_4 \int g^{(4,4,4)}(1,2,3) \nabla_{13} u_p(r_{13}) d\tilde{r}_3. \quad (20)$$

Thus, iterating Eq. (17) we obtain¹¹

$$u^{(4,4)}(r_{12}) = u_p(r_{12}) - \frac{\rho_3}{\rho_4} \frac{Q(r_{12})}{g^{(4,4)}(r_{12})}, \quad (21)$$

with

$$Q(r_{12}) = \rho_4 \sum_{n \geq 0} (-1)^n q_n(r_{12}), \quad (22)$$

$$q_0(r_{12}) = \int g^{(4,4,3)}(1,2,N) \cos(\tilde{r}_{12}, \tilde{r}_{1N}) u^{(4,3)}(r_{1N}) d\tilde{r}_N, \quad (23)$$

$$q_n(r_{12}) = \rho_4 \int \frac{g^{(4,4,4)}(1,2,3)}{g^{(4,4)}(1,3)} \cos(\tilde{r}_{12}, \tilde{r}_{13}) q_{n-1}(r_{13}) d\tilde{r}_3, \quad n > 0. \quad (24)$$

The expectation value of H can now be written as follows

$$\langle H \rangle = (N-1) \mathcal{E}_0(\rho_4) + \mathcal{E}_1(\rho_4), \quad (25)$$

where

$$e_0 = \frac{\hbar^2 \rho_4}{8m_4} \int u_p'(r) g^{(4,4)}(r) d\mathbf{r} + \frac{\rho_4}{2} \int v(r) g^{(4,4)}(r) d\mathbf{r} \quad (26)$$

is the binding energy per particle for a system of pure He^4 at density ρ_4 , and

$$\begin{aligned} e_1 &= e_1^{(1)} + e_1^{(2)} + e_1^{(3)}, \\ e_1^{(1)} &= \frac{\hbar^2 \rho_4}{8m_4} \left\langle \frac{7}{3} \right\rangle \int u^{(4,3)}(r) g^{(4,3)}(r) d\mathbf{r}, \\ e_1^{(2)} &= \rho_4 \int v(r) g^{(4,3)}(r) d\mathbf{r}, \\ e_1^{(3)} &= - \frac{\hbar^2 \rho_4}{8m_4} \int Q(r) \frac{g^{(4,4)}(r)}{g^{(4,4)}(r)} d\mathbf{r}, \end{aligned} \quad (27)$$

is the energy shift caused by the replacement of a He^4 atom by a mass-3 boson: $e_1^{(1)}$ and $e_1^{(2)}$ represent the direct energy of the mass-3 boson in the He^4 medium, and $e_1^{(3)}$ represents the energy shift of the He^4 medium when the latter is perturbed by the presence of a mass-3 boson. It is also clear that $e_1(\rho_4)$ is the binding energy or the chemical potential of one mass-3 boson in liquid He^4 , since

$$e_1(\rho_4) = L \left. \frac{\partial \langle H \rangle}{\partial N_3} \right|_{N_4, \Omega} \quad (28)$$

For one impurity, the statistics of the impurity is irrelevant. Therefore, $e_1(\rho_4)$ is also the binding energy, or the chemical potential, of one He^3 atom in liquid He^4 .

N_3 Mass-3 Bosons in Liquid He^4

Starting with $u_p(r)$ for $u^{(4,4)}(r)$ and the solution $u^{(4,3)}(r)$ of Eq. (18)--now denoted by $u^{(4,3)}_{(0)}(r)$ --for $u^{(4,3)}(r)$, an iterative procedure

can be carried out for Eqs. (12)-(14), solving for $u^{(3,3)}(r)$ and the adjusted $u^{(4,3)}(r)$ and $u^{(4,4)}(r)$. Equations (12)-(14) can be put in a conveniently reduced form:

$$u^{(3,3)}(r_{N-1,N}) = \frac{g^{(3,3)}(r_{N-1,N})}{g^{(3,3)}(r_{N-1,N})} - \rho_4 \int g^{(4,3)}(r_{1,N-1}) g^{(4,3)}(r_{1N}) u^{(4,3)}(r_{1N}) dr_{1N}, \quad (29)$$

$$u^{(4,3)}(r_{1N}) = u^{(4,3)}(r_{1N}) - \frac{\rho_3}{\rho_4} \frac{T(r_{1N})}{g^{(4,3)}(r_{1N})}, \quad (30)$$

and

$$u^{(4,4)}(r_{12}) = u^{(4,4)}(r_{12}) - \frac{\rho_3}{\rho_4} \frac{Q(r_{12})}{g^{(4,4)}(r_{12})} + \left(\frac{\rho_3}{\rho_4}\right)^2 S(r_{12}), \quad (31)$$

where $Q(r_{12})$ has been defined in Eqs. (22)-(24), and $S(r)$ and $T(r)$ are given by

$$S(r_{12}) = \sum_{n \geq 0} (-1)^n s_n(r_{12}), \quad (32)$$

with

$$s_0(r_{12}) = \rho_4 \int \frac{g^{(4,4,3)}(1,2,N)}{g^{(4,3)}(r_{1N})} T(r_{1N}) \cos(r_{12}, r_{1N}) dr_{1N}, \quad (33)$$

$$s_n(r_{12}) = \rho_4 \int \frac{g^{(4,4,4)}(1,2,3)}{g^{(4,4)}(r_{13})} s_{n-1}(r_{13}) \cos(r_{12}, r_{13}) dr_{13}, \quad n > 0, \quad (34)$$

and

$$T(r_{1N}) = \sum_{n \geq 0} (-1)^n t_n(r_{1N}), \quad (35)$$

with

$$t_0(r_{1N}) = \rho_4 \int g^{(4,3,3)}(1,N-1,N) u^{(3,3)}(r_{N-1,N}) \cos(r_{1N}, r_{N-1,N}) dr_{N-1}, \quad (36)$$

$$t_n(r_{1N}) = \rho_4 \int \frac{g^{(r,r,e)}(1,2,N)}{g^{(4,3)}(r_{2N})} t_{n-1}(r_{2N}) \cos(r_{1N}, r_{2N}) dr_{2N}. \quad (37)$$

The formal solution to the equations is thus seen to consist of a very complicated set of coupled recursion relations. The actual process of solving these equations is arduous but straightforward.

In terms of these functions, the expectation value of the Hamiltonian for the binary boson solution finally appears as follows:

$$\begin{aligned} \langle H \rangle &= \frac{\langle \psi_0 | H | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle} \\ &= N_4 e_0(\rho_4) + N_3 e_1(\rho_4) + \frac{N_3^2}{N_4} e_2(\rho_3, \rho_4), \quad (38) \end{aligned}$$

where e_0 and e_1 are as defined earlier in Eqs. (26)-(27), and

$$\begin{aligned} e_2(\rho_3, \rho_4) &= e_2^{(1)} + e_2^{(2)} + e_2^{(3)} + e_2^{(4)}, \\ e_2^{(1)} &= \frac{\hbar^2 \rho_4}{8m_3} \int u^{(3,3)}(r) g^{(3,3)}(r) d\tilde{r}, \\ e_2^{(2)} &= \frac{\rho_4}{2} \int v(r) g^{(3,3)}(r) d\tilde{r}, \\ e_2^{(3)} &= - \frac{\hbar^2 \rho_4}{8\Delta m} \int \frac{g^{(4,3)}(r)}{g^{(4,3)}(r)} T(r) d\tilde{r}, \\ e_2^{(4)} &= - \frac{\hbar^2 \rho_4}{8m_4} \int \frac{g^{(4,4)}(r)}{g^{(4,4)}(r)} S(r) d\tilde{r}, \end{aligned} \quad (39)$$

with

$$\Delta m = \left[\frac{1}{m_3} + \frac{1}{m_4} \right]^{-1}.$$

e_2 can be interpreted as the interaction energy between the mass-3 bosons. $e_2^{(1)}$ and $e_2^{(2)}$ give the direct interaction energy between the mass-3 bosons. $e_2^{(3)}$ describes an indirect contribution through interactions between mass-3 bosons and the He^4 atoms in the background. $e_2^{(4)}$

describes a deformation of the liquid medium. As we shall see in the next section, ϵ_2 is directly related to the long wavelength limit of the effective interaction between He^3 quasiparticles in a realistic $\text{He}^3\text{-He}^4$ solution.

Some of the details left out of this section can be found in the Appendix.

IV. Numerical Results

Numerical computations following the above prescription have been carried out for a 6% solution at an appropriate equilibrium density, $\rho_4 = 0.218 \text{ \AA}^{-3}$. In the two body potential we used the de Boer-Michels parameters, $\epsilon = 10.22^\circ\text{K}$, $\sigma = 2.556 \text{ \AA}$.

The explicit form for the family of pair distribution functions is taken to be

$$\begin{aligned}
 g^{(\alpha,\beta)}(r) &= g_0^{(\alpha,\beta)}(r) + \delta g^{(\alpha,\beta)}, \\
 g_0^{(\alpha,\beta)}(r) &= (C+1) \exp\left[-\left(\frac{d}{r}\right)^{10}\right] - C \exp\left[-(1+z)\left(\frac{d}{r}\right)^{10}\right], \\
 \delta g^{(\alpha,\beta)}(r) &= A\left[\left(\frac{d}{r}\right)^6 \exp\left[-(1+y)\left(\frac{d}{r}\right)^{10}\right] - B\left(\frac{d}{r}\right)^8 \exp\left[-(1+q)\left(\frac{d}{r}\right)^{10}\right]\right], \quad (40)
 \end{aligned}$$

where C , d , A , y and q are variational parameters, and z and B are determined by the normalization conditions, Eq. (8). This form has been found in our previous work⁶ to be flexible and satisfactory for pure helium liquids.

The parameters for $g^{(4,4)}(r)$ were determined in reference 6. The optimum values of the parameters for $g^{(4,3)}(r)$ and $g^{(3,3)}(r)$ are given in Table I. Since at low mass-3 concentrations a simpler form should suffice for $g^{(3,3)}(r)$, we have chosen A to be zero in $g^{(3,3)}(r)$

i.e., $\delta g^{(3,3)}(r) = 0$. As discussed earlier, $g^{(4,4)}(r)$ does not vary when we determine $g^{(4,3)}(r)$; thus the parameters in $g^{(4,3)}(r)$ are determined by minimizing \mathcal{E}_1 , keeping \mathcal{E}_0 fixed. Likewise the parameters in $g^{(3,3)}(r)$ result from a minimization of \mathcal{E}_2 , keeping \mathcal{E}_0 and \mathcal{E}_1 fixed.

The functions $g^{(\alpha,\beta)}(r)$ are plotted in Fig. 1. $g^{(4,3)}(r)$ has the expected behavior. In comparison to $g^{(4,4)}(r)$, its peak is shifted toward larger r , signifying that a mass-3 particle sweeps out a larger volume than a mass-4 particle. Also, the peak for $g^{(4,3)}(r)$ is less pronounced (lower and broader), indicating less localization for a mass-3 boson on account of its larger zero-point motion.

The behavior of $g^{(3,3)}(r)$ is also consistent with physical considerations. In the region $r \lesssim 5.5\text{\AA}$ there is a vanishing probability of finding a mass-3 boson, given one at the origin. This is a manifestation of an excluded volume in the neighborhood of an impurity which results from the interaction of the impurity with the He^4 atoms in the medium: the formation of a single impurity quasiparticle. We do not believe that the near constant region in $g^{(3,3)}(r)$ has any significance: it is an artifact of the restricted analytic form used for the family of trial functions.

The result for \mathcal{E}_1 , the binding energy or chemical potential of one He^3 atom in liquid He^4 , is given in Table 2. It compares favorably with the experimental data of Edwards¹² et al.

To obtain an accurate estimate of the volume excess parameter α in our theory, we need² the knowledge of $\partial\mathcal{E}_1(\rho_4)/\partial\rho_4$ as a function of ρ_4 . Since we have only performed this calculation at one density, we

resort to a much less accurate procedure. Let $r_m^{(\alpha,\beta)}$ be the position of the first maximum in $g^{(\alpha,\beta)}(r)$; then the ratio of effective volumes occupied by a He^3 and a He^4 atom is approximately given by¹³

$$1 + \alpha \approx \left[\frac{2r_m^{(4,3)} - r_m^{(4,4)}}{r_m^{(4,4)}} \right]^3. \quad (41)$$

With $r_m^{(4,4)} \approx 3.37\text{\AA}$ and $r_m^{(4,3)} \approx 3.54\text{\AA}$, we obtain $\alpha \approx 0.33$ not inconsistent with the experimental values, $\alpha = 0.284 - 0.301$.¹⁴ In an earlier paper,¹⁵ we actually computed α from $\partial \mathcal{E}_1(\rho_4)/\partial \rho_4$. The value obtained was much more reliable, even though the values of $\mathcal{E}_1(\rho_4)$ are not as satisfactory. In our present calculation the inclusion of proper correlations leads to a significantly improved value of \mathcal{E}_1 at $\rho_4 = 0.0218\text{\AA}^{-3}$. We are confident that similar improvement in α will be found if properly computed from $\partial \mathcal{E}_1(\rho_4)/\partial \rho_4$. However the amount of computer time required prevents us from carrying out a thorough investigation. The results of our previous work as well as results obtained by Davison and Feenberg¹⁶ from a second order perturbation calculation are included in Table 2 for comparison.

The significance of α is that it is related directly to the long wavelength limit of the effective interaction, V_0 , between two He^3 quasi-particles in the dilute He^3 - He^4 solution. For, varying the ground state energy with respect to the number density of the mass-3 bosons, we obtain the chemical potential of a mass-3 boson in the solution at finite concentrations; and the variation of this chemical potential with respect to the number density of mass-3 bosons, holding the chemical potential of He^4 constant, leads to V_0 . Starting with Eq. (38), we obtain first the chemical potential. To first order in the concentration x ,

$$\begin{aligned} \mu_3(N_3, N_4, \Omega) &= \left(\frac{\partial(H)}{\partial N_3} \right)_{N_4, \Omega} \\ &= e_1(\rho_4) + 2\alpha e_2(\rho_3, \rho_4) . \end{aligned} \quad (42)$$

Next,

$$\begin{aligned} v_o &= \left(\frac{\partial \mu_3}{\partial \rho_3} \right)_{\mu_4} \\ &= \frac{\partial e_1}{\partial \rho_4} \left(\frac{\partial \rho_4}{\partial \rho_3} \right)_{\mu_4} + \frac{2}{\rho_4^o} e_2(\rho_3, \rho_4) \\ &= - (1 + \alpha) \left(\frac{\partial e_1}{\partial \rho_4} \right)_{\rho_4^o} + \frac{2}{\rho_4^o} e_2(\rho_3, \rho_4) . \end{aligned} \quad (43)$$

ρ_4^o is the density of pure He^3 at the same pressure (assumed zero) as the solution. In comparison to the expression for v_o derived by Bardeen, Baym and Pines¹:

$$v_o^{\text{BBP}} = - (1 + \alpha)^2 \frac{m_4 s^2}{\rho_4^o} + (1 + 2\alpha) \frac{m_4 s^2}{\rho_4^o} , \quad (44)$$

where s is the velocity of sound in pure He^3 at the same pressure as the solution, we note that the first term in Eq. (43) represents the phonon-induced contribution to v_o , and the second term the direct contribution. In fact we find the relations:

$$\left(\frac{\partial e_1}{\partial \rho_4} \right)_{\rho_4^o} = (1 + \alpha) \frac{m_4 s^2}{\rho_4^o} , \quad (45)$$

and

$$2e_2(\rho_3, \rho_4) = (1 + 2\alpha)m_4 s^2 . \quad (46)$$

Equation (45) shows, as discussed earlier, how α may be computed from $\partial \mathcal{E}_1 / \partial \rho_4$, if the latter information were available. Equation (46) provides an alternate procedure which extracts α from \mathcal{E}_2 . However, on account of the combination $(1 + 2\alpha)$, this procedure is not expected to be quantitatively useful. Our variational calculation gives an upper bound of 24.06°K for \mathcal{E}_2 , (Table 2) corresponding to $\alpha = 0.38$. The experimental value of α , 0.284, corresponds to $\mathcal{E}_2 = 21.6$. While a 10% discrepancy in the variational determination of \mathcal{E}_2 needs no apology, its inferred value of α certainly contains intolerably magnified errors. Our hope of a sensitive determination of α rests with Eq. (45).

V. Errors and Approximations

The use of the superposition approximation for the three particle distribution function is the major approximation in the calculation. An indication of the size of the error introduced into our results by the use of this approximation can be obtained by comparisons with the results of Monte-Carlo or molecular-dynamics calculations. Unfortunately, at this time calculations of the latter type do not exist for the mass-3 boson-mass-4 boson mixture.¹⁰ However, in ref. (6) a detailed comparison of MD, MC, and SA calculations was made for pure systems of He⁴ and mass-3 bosons. On the basis of these calculations we expect that the error in the energies $\mathcal{E}_1(\rho_4)$ and $\mathcal{E}_2(\rho_3, \rho_4)$ is approximately a half a degree (.5°K). [See also ref. (17,18) for further support of this conclusion.] A measure of the error due to numerical solution of the coupled integral equation is given by the quantity δ , defined in the appendix. This gives a limit of error for any one term in $\mathcal{E}_1(\rho_4)$ and $\mathcal{E}_2(\rho_3, \rho_4)$. $\mathcal{E}_1(\rho_4)$ consists of three terms.

The potential energy is evaluated exactly (see ref (6)). Thus the numerical errors affects only the terms $\mathcal{E}_1^{(1)}$ and $\mathcal{E}_1^{(2)}$. In $\mathcal{E}_2(\rho_3, \rho_4)$ the error affects only $\mathcal{E}_2^{(1)}$, $\mathcal{E}_2^{(2)}$, and $\mathcal{E}_2^{(3)}$.

For $\delta = 0.1\%$, the limit of error in \mathcal{E}_1 is $\sim 1\%$ (1.3%) and $\mathcal{E}_2 \sim 0.5\%$.

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Appendix: Solution of the Coupled Integral Equations

The set of coupled integral equations (12)-(14) for $u^{(4,4)}(r)$, $u^{(4,3)}(r)$, and $u^{(3,3)}(r)$ are solved by an iteration procedure defined as follows:

i) For a given $g^{(4,4)}(r)$ and $g^{(4,3)}(r)$ equations (18) and (17) are solved for $u'_p(r)$ and $u'_o^{(4,3)}(r)$ using the procedure discussed in the appendix of ref. (6);

ii) Defining $q_o(r_{12})$ by Eq. (23) we write (17) (using the SA);

$$u^{(4,4)}(r_{12}) = \frac{g^{(4,4)}(r_{12})}{g^{(4,4)}(r_{12})} - \rho_4 \int g^{(4,4)}(r_{23}) g^{(4,4)}(r_{13}) \times \\ u^{(4,4)}(r_{13}) \cos(12,13) d\bar{r}_3 - \frac{\rho_3}{\rho_4} \frac{q_o(r_{12})}{g^{(4,4)}(r_{12})}. \quad (A1)$$

Direct iteration of this equation, using $u'_p(r)$ as a starting approximation, yields the solution

$$u'_o^{(4,4)}(r_{12}) = u'_p(r_{12}) - \frac{\rho_3}{\rho_4} \frac{Q(r_{12})}{g^{(4,4)}(r_{12})}. \quad (A2)$$

iii) For the same $g^{(4,4)}(r)$ and $g^{(4,3)}(r)$ and a given $g^{(3,3)}(r)$, Eqs. (12)-(14) are solved by direct iteration, using $u'_o^{(4,3)}(r)$ and $u'_p(r)$ as starting approximations. Terms which contribute to the energy in orders higher than x^2 are neglected. Direct substitution of Eqs. (12)-(14) in Eqs. (10)-(11) for $\langle H \rangle$ shows that the term in Eq. (14) involving $g^{(3,3,3)}(N-2, N-1, N)$ contributes to $\langle H \rangle$ only in order x^3 . Equations (12)-(14) are then written

$$u^{(3,3)}(r_{N-1,N}) = \frac{g^{(3,3)}(r_{N-1,N})}{g^{(3,3)}(r_{N-1,N})} - \rho_4 \int g^{(4,3)}(1,N-1) g^{(4,3)}(1N) \\ \times u_0^{(4,3)}(r_{1N}) \cos(N-1,N,1N) d\vec{r}_1 \quad (A3)$$

$$u^{(4,3)}(r_{1N}) = \frac{g^{(3,4)}(r_{1N})}{g^{(3,4)}(r_{1N})} - \rho_4 \int g^{(4,4)}(r_{12}) g^{(4,3)}(r_{2N}) u^{(4,3)}(r_{2N}) \\ \times \cos(1N,2N) d\vec{r}_2 - \frac{\rho_3}{\rho_4} \frac{t_0(r_{1N})}{g^{(3,4)}(r_{1N})} \quad (A4)$$

where $t_0(r_{1N})$ is defined by Eq. (36). (A3) can be solved immediately for $u^{(3,3)}(r)$, since $u_0^{(4,3)}(r)$ is known from step ii). (Contributions to $u^{(3,3)}(r)$ from higher order terms in $u^{(4,3)}(r)$ contribute to $\langle H \rangle$ in order x^3 .) Direct iteration of (A4), using $u_0^{(4,3)}(r)$ as a starting approximation yields Eq. (30). The solution of Eq. (12) for $u^{(4,4)}(r)$ then follows from the procedure used in step i) for $u_0^{(4,4)}(r)$, with $u_0^{(4,3)}(r)$ replaced by $u^{(4,3)}(r)$. This gives Eq. (31).

Transformation of the equations to bi-polar coordinates⁶ results in forms which are easily adaptable to solution by computer.

The numerical precision of the solutions is determined by the accuracy to which the energies are required. Denoting by $\mathcal{E}^{(I)}$ any one of the terms in $\mathcal{E}_1(\rho_4)$ or $\mathcal{E}_2(\rho_3, \rho_4)$, which results from the I^{th} iteration of the equations, we required

$$\left| \frac{\mathcal{E}^{(I+1)} - \mathcal{E}^{(I)}}{\mathcal{E}^{(I)}} \right| \times 100 < \delta, \quad (A5)$$

$\delta = 0.1$. Typical values of I were from 25 to 30.

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Table Captions

Table I. Optimum variational parameters for $g^{(4,4)}(r)$, $g^{(4,3)}(r)$ and $g^{(4,3)}(r)$. A is identically zero for $g^{(3,3)}(r)$.

Table II. The binding energy of one He^3 in He^4 , \mathcal{E}_1 , the mass-3 boson interaction energy \mathcal{E}_2 , and the volume exclusion parameter α . The subscript MW refers to the results of ref. (15) and D to ref. (16). The experimental value of \mathcal{E}_1 is from ref. (12).

Figure Caption

The radial distribution functions $g^{(4,4)}(r)$, $g^{(4,3)}(r)$ and $g^{(3,3)}(r)$ for a 6% solution of mass-3 bosons in He^4 .

Table I

(α, β)	c	d \hat{A}	A	q	y
(4,4)	0.1184	2.459	2.55	462	9.6
(4,3)	0.0225	2.486	2.30	1200	11.5
(3,3)	-0.500	2.312	0.0	----	----

Table II

$e_1^{(1)}$ °K	$e_1^{(2)}$ °K	$e_1^{(3)}$ °K	e_1 °K	e_1^{exp} °K
31.46	-39.42	-5.17	- 2.79	- 2.76
$e_2^{(1)}$ °K	$e_2^{(2)}$ °K	$e_2^{(3)}$ °K	$e_2^{(4)}$ °K	e_2 °K
10.70	- 7.39	- 6.58	14.17	24.06
α	α_{MW}	α_{D}	$e_{1\text{MW}}$ °K	$e_{1\text{D}}$ °K
-0.33	0.31	0.295	- 1.28	- 1.61

