

## Ground State of Liquid Helium (Mass 4)\*

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The wave function describing the ground state of a boson system is approximated by the function  $\Psi = \Pi \exp[\frac{1}{2}u(r_{ij})]$ . The superposition approximation is then used to derive a linear, inhomogeneous integral equation for  $du/dr$  in which the only other quantities occurring are the experimentally observed two-particle distribution function  $g(r)$  and its first derivative. A numerical solution for  $\text{He}^4$  is computed and compared with the explicit approximate solution derived by Abe. Using the computed  $u(r)$  and a proper smooth extrapolation of  $g(r)$  into the region below the apparent cutoff at  $r=2.34$  A, the kinetic energy of liquid  $\text{He}^4$  at absolute zero is estimated at  $2.91 \times 10^{-15}$  ergs/atom.

A functional  $J(du/dr)$  is constructed with the property that

Abe's integral equation for  $du/dr$  is just the Euler equation associated with the problem of finding a  $u$  for which  $J$  takes on an extreme value. The extreme value of  $J$  (actually a maximum) is simply related to the expectation value of the kinetic energy. The variational property is used to determine the best  $u(r)$  from a family of trial functions.

The calculated value of the kinetic energy and the measured total energy are used, in conjunction with the virial theorem, to determine the coefficients of a 6- $n$  Lennard-Jones potential. At  $n=12$ , the calculation yields a deeper potential well and a slightly wider repulsive region than is calculated from the properties of the gas phase.

### I. INTRODUCTION

A TRIAL wave function consisting of a product of two-particle correlation factors appears to provide a reasonably good description of liquid helium II at absolute zero. Abe<sup>1,2</sup> has recently developed a powerful technique for deriving physical consequences from this description with only observed quantities appearing in the final formulas. The present note is devoted first to the further development of Abe's relations. Some consequences of the virial theorem are developed in Sec. IV.

The wave function

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

is used to describe the ground state of an  $N$ -particle boson system confined to the volume  $\Omega$ , where  $r_{ij}$  is the distance between the  $i$ th and  $j$ th particles,  $u(0) = -\infty$ , and  $u(\infty) = 0$ .

We need the two- and three-particle distribution functions

$$\rho_2(r_{12}) \equiv \rho g(r_{12}) \equiv \Omega(N-1) \int |\Psi|^2 d\mathbf{r}_3 d\mathbf{r}_4 \cdots d\mathbf{r}_N / \int |\Psi|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_N, \quad (2)$$

$$\rho_3(1,2,3) \equiv \Omega(N-1)(N-2) \int |\Psi|^2 d\mathbf{r}_4 \cdots d\mathbf{r}_N / \int |\Psi|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_N, \quad (3)$$

in which  $\rho \equiv N/\Omega$  is the mean-particle density. The function  $g(r)$  is subjected to boundary conditions  $g(0) = 0$ ,  $g(\infty) = 1$ , and the normalization condition

$$\rho \int [g(r) - 1] d\mathbf{r} = -1. \quad (4)$$

Also

$$g(r) = 1 + \frac{1}{8\pi^3 \rho} \int [S(k) - 1] e^{-ik \cdot r} d\mathbf{k} \quad (5)$$

gives  $g(r)$  in terms of the liquid structure factor  $S(k)$ , a quantity determined experimentally by analysis of x-ray diffraction patterns.

Formulas involving  $\rho_3$  are evaluated by introducing the superposition approximation,

$$\rho_3(1,2,3) \cong \rho^2 g(r_{12}) g(r_{23}) g(r_{31}). \quad (6)$$

In our calculation, experimental values of  $S(k)$  for liquid  $\text{He}^4$  in the ground state are taken from Goldstein and Reekie<sup>3</sup> after imposing the normalization suggested by Feynman and Cohen<sup>4</sup>; namely, multiplication by a factor 0.97 throughout and linear extrapolation near the origin to  $S(0) = 0$ . The function  $g(r)$  and its derivative are calculated from Eq. (5). Because of the limitation of experimental data, we follow Goldstein in setting  $S(k) = 1$ ,  $k > 6 \text{ \AA}^{-1}$ . From the definition  $g(r) \geq 0$ ; however the cutoff in wave number space has the consequence that the computed  $g(r)$  approaches the axis sharply and crosses at  $r \cong 2.34$  A. Below  $r = 2.34$  A, Eq. (5) must be replaced by  $g(r) = 0$ .

### II. BASIC RELATIONS

The Hamiltonian of the system is

$$H = T + V,$$

where

$$T = -\frac{\hbar^2}{2M} \sum_i \Delta_i, \quad (7)$$

$$V = \sum_{i < j} V(r_{ij})$$

are the kinetic energy and potential energy operators, respectively.

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<sup>1</sup> R. Abe, Progr. Theoret. Phys. (Kyoto) **19**, 57 (1958).

<sup>2</sup> R. Abe, Progr. Theoret. Phys. (Kyoto) **19**, 407 (1958).

<sup>3</sup> L. Goldstein and J. Reekie, Phys. Rev. **98**, 857 (1955).

<sup>4</sup> R. P. Feynman and M. Cohen, Phys. Rev. **102**, 1189 (1956).

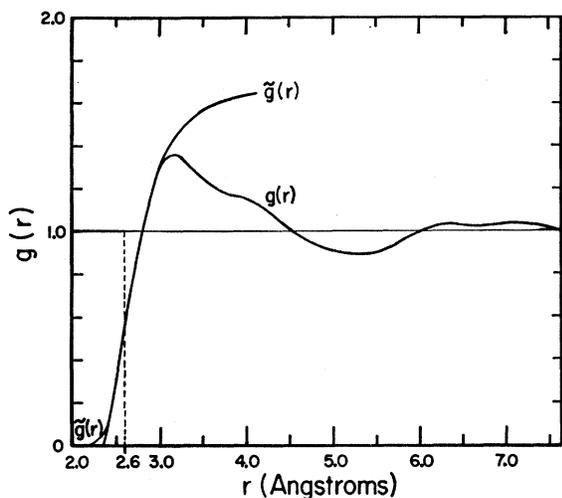


FIG. 1. The two-particle distribution function.

Using the wave function (1), the expectation value of the K. E. operator is readily reduced to the form

$$\langle T \rangle = N\rho \frac{\hbar^2}{8M} \int g'(r)u'(r)dr. \quad (8)$$

Also

$$\langle V \rangle = \frac{1}{2}N\rho \int g(r)V(r)dr. \quad (9)$$

An equation expressing  $u(r)$  in terms of  $g(r)$  can be derived by computing  $\nabla_{12}g(r_{12})$  from Eq. (2). With the help of Eq. (3) and the superposition approximation

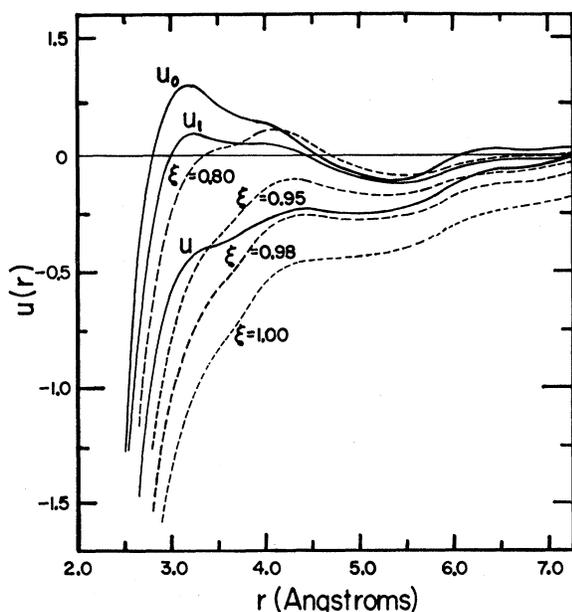


FIG. 2. Solutions of Eq. (11):  $u_0 = \ln g(r)$ , zeroth approximation;  $u_1$ , first approximation;  $u$ , exact solution. Curves in dashed lines are computed from Eq. (12).

Eq. (6), the resulting equation is

$$\nabla_{12}g(r_{12}) = g(r_{12})\nabla_{12}u(r_{12}) + \rho g(r_{12}) \int g(r_{23})g(r_{31})\nabla_{12}u(r_{31})dr_3, \quad (10)$$

which is equivalent to the scalar equation

$$g'(r_{12}) = g(r_{12})u'(r_{12}) + \rho g(r_{12}) \int g(r_{23})g(r_{31})u'(r_{31}) \times \cos(12,13)dr_3. \quad (11)$$

Equation (11) is a linear inhomogeneous integral equation for  $u'(r)$ . Abe obtains a formal solution in the form of an infinite series by a process of iteration. Each term in the series can be represented by a cluster diagram of a simple closed loop and a complete set of cross links radiating from particle 1. The approximation of replacing  $g(r_{1n})$  by a constant  $\xi \leq 1$  in all the cross links leaves a form which can be summed. The resulting formula is

$$u(r) = \ln g(r) - \frac{1}{8\pi^3\rho} \int \frac{[S(k)-1]^2}{1+\xi[S(k)-1]} e^{-ik \cdot r} dk. \quad (12)$$

Abe's approximation results from setting  $\xi = 1$ .

Equation (12) has been integrated for  $\xi = 1, 0.98, 0.95,$  and  $0.80$ , with the results shown as the curves in broken lines in Fig. 2. We have also computed essentially the exact solution by setting up the iteration procedure on a high speed computer. The  $u(r)$  found in this manner is shown in Fig. 2. It is seen that the approximation represented by Eq. (12) is best when  $\xi$  is somewhat smaller than 1. Furthermore the solution corresponding to the approximation of retaining only the first term in the iteration series is also shown in Fig. 2. Apparently both the approximations of setting  $\xi = 1$  and of retaining only the first term of the iteration series are inadequate if our purpose is to compute  $u(r)$  accurately.

The kinetic energy is calculated by inserting Eq. (11) into Eq. (8). We get

$$\langle T \rangle = N\rho \frac{\hbar^2}{8M} (J_a + J_b), \quad (13)$$

where

$$J_a = \int (g'^2/g)dr,$$

$$J_b = -\rho \int g(r_{12})dr_2 \int g(r_{23})g(r_{31})u'(r_{31}) \cos(12,13)dr_3.$$

The integrand of  $J_a$  is poorly defined below  $r = 2.4$  A by the available information on  $g(r)$ . We have tried to obtain a reasonable estimate by using the function

$$\tilde{g}(r) = g(d) \exp\{\lambda[1 - (d/r)^n]\} \quad (14)$$

TABLE I. Estimate of kinetic energy.

$d$ (A)	$g(d)d$	$\lambda$	$n$	$4\pi \int_0^d (g'^2/g)r^2 dr$	$J_a$	$J_b$	$\langle T \rangle / N$ ( $10^{-15}$ erg/atom)
2.6	1.381	1.125	11.0	380	598	42	2.91
2.5	0.715	1.320	15.4	308	649	42	3.15
2.4	0.184	1.203	47.2	237	783	42	3.76

to extrapolate  $g(r)$  below  $r=d$ . The parameters  $\lambda$  and  $n$  are chosen so that we have  $\tilde{g}'(d)=g'(d)$  and  $\tilde{g}''(d)=g''(d)$ . Using Eq. (14) we find

$$4\pi \int_0^d (g'^2/g)r^2 dr = 4\pi g(d)d \left[ n\lambda + n - 1 - (n-1) \times \int_0^1 \exp[\lambda(1-1/x^n)] dx \right]. \quad (15)$$

Numerical results are collected in Table I.

Curve  $\tilde{g}(r)$  for  $d=2.6$  A exhibits the excellent fit to  $g(r)$  up to  $r=3$  A as shown in Fig. 1. The corresponding extrapolation function for  $d=2.4$  A is unsatisfactory because it falls below  $g(r)$  in the range  $2.34 \text{ A} \leq r < 2.40 \text{ A}$ . This behavior permits the conclusion that the last row of Table I provides a safe upper limit on the true value of the integral and, therefore, a safe upper limit on the kinetic energy. In the following calculations we have extrapolated  $g(r)$  by Eq. (14) for  $d=2.6$  A.

### III. EQUATION (11) AS AN EXTREMUM CONDITION

Equation (11) is exactly the condition for giving an extreme value to the integral

$$J = - \int g(r_{12}) [u'(r_{12})]^2 d\mathbf{r}_2 + 2 \int g'(r_{12}) u'(r_{12}) d\mathbf{r}_2 - \rho \int g(r_{12}) g(r_{23}) g(r_{31}) u'(r_{12}) u'(r_{31}) \times \cos(12,13) d\mathbf{r}_2 d\mathbf{r}_3 \quad (16)$$

as a functional in  $u'(r)$ . Our numerical results in Table II are consistent with the extremum being actually a maximum. This extremum property permits us to choose from a family of particular trial functions the best approximation to  $u(r)$ . Introducing Eq. (11) into Eq.

TABLE II. Evaluation of Eq. (20) for  $u(r) = -(b/r)^m$ .

$m$	$b = (\gamma_{\text{ext}})^{1/m}$ (A)	$J_{\text{ext}}$ (A)	$\langle T \rangle / N$ ( $10^{-15}$ erg/atom)
4	3.41	455	2.07
5	3.14	505	2.30
6	2.98	545	2.48
7	2.87	575	2.62
8	2.80	596	2.72
9	2.74	608	2.77
10	2.69	612	2.79
11	2.65	610	2.78

(16), the extreme value is

$$J_{\text{ext}} = \int g'(r_{12}) u'(r_{12}) d\mathbf{r}_2, \quad (17)$$

consequently by Eq. (8),

$$\langle T \rangle = N\rho(\hbar^2/8M)J_{\text{ext}}. \quad (18)$$

The form of  $J$  in Eq. (16) permits the introduction of an amplitude parameter  $\gamma$  in conjunction with any trial function  $u(r)$ . Thus we write

$$J(\gamma) = 2\gamma J_1 - \gamma^2 J_2,$$

with

$$J_1 = \int g'(r) u'(r) d\mathbf{r} = - \int g(r) \Delta u(r) d\mathbf{r},$$

$$J_2 = \int g(r) [u'(r)]^2 d\mathbf{r} + \rho \int g(r_{12}) g(r_{23}) g(r_{31}) u'(r_{12}) u'(r_{31}) \times \cos(12,13) d\mathbf{r}_2 d\mathbf{r}_3,$$

and obtain

$$\gamma_{\text{ext}} = J_1/J_2, \quad (20)$$

$$J_{\text{ext}} = J(\gamma_{\text{ext}}) = J_1^2/J_2.$$

To illustrate the usefulness of Eqs. (18)–(20), the integrals  $J_1$  and  $J_2$  have been evaluated for the trial function  $u(r) = -(b/r)^m$ . The results are shown in Table II. A maximum value of  $J_{\text{ext}}$  is observed at  $m=10$  which gives  $u(r) = -(2.69 \text{ A}/r)^{10}$  as the best approximation to the solution of Eq. (11) for this particular family of trial functions. This result is numerically

TABLE III. Evaluation of Eq. (23).

$n$	$C_n$ ( $\text{A}^{-n}$ )
6	$3.042 \times 10^{-8}$
8	$2.830 \times 10^{-4}$
9	$9.254 \times 10^{-5}$
10	$3.115 \times 10^{-5}$
11	$1.072 \times 10^{-5}$
12	$3.759 \times 10^{-6}$
13	$1.338 \times 10^{-6}$
14	$4.832 \times 10^{-7}$

TABLE IV. Evaluation of the potential.

$n$	$\alpha$ ( $10^{-10}$ erg-A $^n$ )	$\beta$ ( $10^{-10}$ erg-A $^6$ )	$\sigma$ (A)	$\epsilon$ ( $10^{-15}$ erg)	$r^*$ (A)	$\epsilon^*$ ( $10^{-15}$ erg)	$M\epsilon^*r^{*2}/\hbar^2$
8	0.309	0.0415	2.728	2.52	3.150	1.06	6.30
9	0.630	0.0319	2.702	2.05	3.093	1.21	6.94
10	1.40	0.0271	2.682	1.82	3.047	1.36	7.56
11	3.26	0.0243	2.665	1.69	3.009	1.49	8.08
12	7.75	0.0223	2.651	1.61	2.975	1.61	8.52
	[4.388]	[0.01574]	[2.556]	[1.411]	[2.869]	[1.411]	[6.96]
13	18.7	0.0210	2.638	1.55	2.946	1.73	9.00
14	45.2	0.0199	2.627	1.52	2.920	1.84	9.37

consistent with the zeroth order approximation of Eq. (11), namely  $g'(r) = g(r)u'(r)$ , in the region where Eq. (14) is used for  $g(r)$ . For  $m=4$ ,  $\gamma_{\text{ext}}$  has also been computed by a cluster expansion procedure using a Lennard-Jones 6-10 potential.<sup>5</sup> The result is  $b=2.92$  A, not far from corresponding value in Table II.

A fairly general trial function results from introducing two amplitude parameters into the right-hand member of Eq. (12). The resulting variational problem exhibits an extensive and very flat plateau in the parameters and the variable  $\xi$ . The best value of the kinetic energy is  $2.85 \times 10^{-15}$  erg/atom.

#### IV. VIRIAL THEOREM AND THE 6- $n$ LENNARD-JONES POTENTIAL

In this section we determine the relations connecting the range and depth of a 6- $n$  Lennard-Jones potential with the energy per atom  $\mathcal{E}_0 (= -0.97 \times 10^{-15}$  erg/atom $^6$ ) and the kinetic energy per atom  $T_0$  (estimated at  $2.91 \times 10^{-15}$  erg/atom in Table I). The connection is made by employing the two-particle distribution function  $g(r)$  to compute the expectation values of the potential energy. The assumed potential is written

$$V(r) = (\alpha/r^n) - (\beta/r^6) \equiv 4\epsilon[(\sigma/r)^n - (\sigma/r)^6] \\ \equiv [\epsilon^*/(n-6)][6(r^*/r)^n - n(r^*/r)^6], \quad (21)$$

where  $r^*$  is the separation at minimum potential and  $-\epsilon^*$  the depth at the minimum.

We start from the trial wave function  $\Psi_0(\lambda \mathbf{r}_1, \dots, \lambda \mathbf{r}_N)$  generated by introducing a scale parameter  $\lambda$  into the normalized ground-state eigenfunction at zero pressure. The expectation value of the energy is then given by

$$E(\lambda)/N = \lambda^2 T_0 + \epsilon^*(6r^{*n}\lambda^n C_n - nr^{*6}\lambda^6 C_6)/(n-6), \quad (22)$$

in which

$$C_n = 2\pi\rho \int_0^\infty g(r)r^{2-n}dr \quad (23)$$

is given in Table III for  $n=6, 8, 9, \dots, 14$ .

<sup>5</sup> Clayton Williams (private communication).

<sup>6</sup> K. R. Atkins, *Liquid Helium* (Cambridge University Press, New York, 1959), p. 22.

The parameters  $r^*$  and  $\epsilon^*$  are now determined by the conditions  $E(1) = N\mathcal{E}_0$ , and  $\partial E(\lambda)/\partial \lambda = 0$  at  $\lambda=1$  (the virial theorem for zero pressure). Thus

$$r^{*n}\epsilon^* = (2T_0 - 3\mathcal{E}_0)/3C_n, \\ r^{*6}\epsilon^* = [(n-2)T_0 - n\mathcal{E}_0]/nC_6. \quad (24)$$

The parameters  $r^*$  and  $\epsilon^*$ , hence  $\alpha, \beta, \sigma$ , and  $\epsilon$ , computed from Eq. (24) appear in Table IV.

Values of these parameters are known for  $n=12$  computed by quantum mechanics<sup>7</sup> from the properties of the gas phase. These values appear in brackets in Table IV. Unfortunately the corresponding parameters have not been computed for other values of  $n$ . The discrepancy at  $n=12$  is substantial. A smaller value for  $T_0$  (say  $2.50 \times 10^{-15}$  erg/atom) does not bring agreement;  $\epsilon^*$  is reduced, but  $r^*$  is increased by the change. It is also noteworthy that  $r^*$  is quite insensitive to small variations in  $\mathcal{E}_0$ ;  $\epsilon^*$  is also insensitive, but to a lesser degree.

An informative comparison is possible, at  $n=10$ , with the critical potential which just fails to possess a bound state. Under this condition the two-particle eigenfunction for the zero-energy  $S$  state is exactly

$$\psi(r) = \frac{1}{r} \exp[-\frac{3}{4}(r^*/r)^4]. \quad (25)$$

One finds easily that Eq. (25) satisfies the Schrödinger equation

$$\left\{ -\frac{\hbar^2}{M}\Delta + \frac{3\hbar^2}{2Mr^{*2}} \left[ 6\left(\frac{r^*}{r}\right)^{10} - 10\left(\frac{r^*}{r}\right)^6 \right] \right\} \psi(r) = 0. \quad (26)$$

Thus

$$[M\epsilon^*r^{*2}/\hbar^2]_{\text{critical}} = 6.$$

The corresponding number from the analysis of the liquid state is (from Table IV)

$$M\epsilon^*r^{*2}/\hbar^2 = 7.56.$$

<sup>7</sup> R. B. Bird, J. O. Hirschfelder, and C. F. Curtiss, *Handbook of Physics* (McGraw-Hill Book Company, New York, 1958), Part 5, Chap. 4, Table 4.1.