

Ground State of Liquid He^{4†}

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The properties of the ground state of liquid He⁴ are studied using a variational wave function of the form $\prod_{i<j} f(r_{ij})$. The Lennard-Jones 12-6 potential is used with parameters determined from the gas data by deBoer and Michiels. The configuration space integrals are performed by a Monte Carlo technique for 32 and 108 atoms in a cube with periodic boundary conditions. With $f(r) = \exp[-(2.6 \text{ \AA}/r)^6]$, the ground-state energy is found to be -0.78×10^{-15} ergs/atom, which is 20% above the experimental value. The liquid structure factor and the two-particle correlation function are in reasonably good agreement with the x-ray and neutron scattering experiments.

INTRODUCTION

THE interacting Bose gas¹⁻⁵ has been the subject of intensive theoretical investigation as a microscopic model for the behavior of liquid He⁴. Successful calculations have been performed for the Bose gas with weak repulsive interactions¹ and for the low-density Bose gas with short-range repulsive interactions.² This work provides a beautiful model of the superfluid behavior of the interacting Bose gas and of the existence of phonons and quantized vortices, but it does not permit one to perform quantitative calculations for liquid He⁴.

A variational method⁶⁻⁹ in which the trial wave function is expressed as a product of pair functions [see Eq. (3)] has been used extensively to describe the ground state of the interacting Bose system. This method can be applied directly to the intermediate density hard-sphere gas or to a realistic Hamiltonian for liquid He⁴. In this paper we report the quantitative calculation of the properties of the ground state of liquid He⁴ using this variational method.

THEORY

We will consider N helium atoms of mass m in a cubic box of volume Ω interacting through the two-body potential $V(r)$.

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i<j=1}^N V(r_{ij}). \quad (1)$$

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¹ N. Bogoliubov, J. Phys. (USSR) **11**, 23 (1947).

² T. D. Lee, K. Huang, and C. N. Yang, Phys. Rev. **106**, 1135 (1957).

³ K. A. Brueckner and K. Sawada, Phys. Rev. **106**, 1117 (1957); **106**, 1128 (1957).

⁴ S. T. Beliaev, Zh. Eksperim. i Teor. Fiz. **34**, 417 (1958); **34**, 433 (1958) [English transl.: Soviet Phys.—JETP **7**, 289 (1958); **7**, 299 (1958)].

⁵ N. M. Hugenholtz and D. Pines, Phys. Rev. **116**, 489 (1959).

⁶ N. F. Mott, Phil. Mag. **40**, 61 (1949).

⁷ R. B. Dingle, Phil. Mag. **40**, 573 (1949).

⁸ R. Jastrow, Phys. Rev. **98**, 1479 (1955).

⁹ J. B. Aviles, Jr., Ann. Phys. (N.Y.) **5**, 251 (1958).

Estimates of the potential have been made theoretically from the atomic structure of helium and empirically from the gas kinetic data. Theoretically, it consists of two parts: the attractive Van der Waals interaction at^{10,11} large r and the repulsive Coulomb and exchange interactions¹² for small r , where the wave functions of the two atoms overlap appreciably. deBoer and Michiels¹³ have obtained an empirical interaction by fitting the parameters of the Lennard-Jones 12-6 potential to the experimental values of the second virial coefficient above 60°K. They found

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6],$$

$$\epsilon = 10.22^\circ\text{K}, \quad (2)$$

$$\sigma = 2.556 \text{ \AA}.$$

Using this potential, Kilpatrick *et al.*¹⁴ calculated the second virial coefficient from 2 to 60°K and found a good fit to the experimental data in that temperature range. This form for the potential is convenient and it is used in the present calculation. More recent measurements at low temperatures by Keller¹⁵ indicate that the potential should be somewhat more attractive.

The trial wave function may be formulated in the following way. In order to obtain a reasonable value for $\langle V \rangle$ in the many-body system, the wave function must be small whenever the potential is large, that is, whenever any two particles are less than 2.6 Å apart. This can be accomplished by choosing the trial wave function to be a product of pair functions, the product being taken over all pairs.

$$\psi = \prod_{i<j=1}^N f(r_{ij}), \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|. \quad (3)$$

The pair function can then be made small for $r < 2.6 \text{ \AA}$ and should approach a constant for large r .

¹⁰ J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

¹¹ H. Margenau, Phys. Rev. **56**, 1000 (1939).

¹² J. C. Slater, Phys. Rev. **32**, 349 (1928).

¹³ J. deBoer and A. Michiels, Physica **5**, 945 (1938); **6**, 97 (1939).

¹⁴ J. E. Kilpatrick, W. E. Keller, E. F. Hammel, and N. Metropolis, Phys. Rev. **94**, 1103 (1954).

¹⁵ J. E. Kilpatrick, W. E. Keller, and E. F. Hammel, Phys. Rev. **97**, 9 (1955).

Since we are dealing with bosons, the wave function should be totally symmetric under exchange of any two-particle coordinates; the trial function has the proper symmetry.

Although this form for the wave function is simple, it has two very interesting properties. First of all, Bogoliubov and Zubarev¹⁶ have shown that in the weak coupling limit the exact ground-state wave function can be written in this form. Hiroike¹⁷ has shown that this trial wave function will reproduce the first two terms in the low-density expansion of the ground-state energy of the hard-sphere gas. Secondly, we expect the probability distribution function

$$P_N(\mathbf{r}_1 \cdots \mathbf{r}_N) = \psi^2(\mathbf{r}_1 \cdots \mathbf{r}_N) = \prod_{i < j} f^2(r_{ij}) / \int \prod f^2 \quad (4)$$

to exhibit at least two phases: a disordered (gas or liquid) phase at low densities, and an ordered, solid phase at high densities (since the classical system with $\exp[-V(r_{ij})/kT] = f^2(r_{ij})$ is expected to have this behavior). Thus, the trial wave function (3) should give good results for the ground state of the low-density gas and may provide a useful variational wave function for the intermediate-density gas (or liquid) and for the solid.

We must now choose a reasonable form for the pair function which contains variable parameters. This function should be small for small r where the potential is large and should approach a constant for large r . At small distances where the two particles interact strongly the pair function is not expected to be very different from the solution of the two-body problem. The numerical technique which we will use to evaluate the integrals places a severe restriction on the range of the pair function, namely, that the pair function be sensibly constant for r greater than $\approx 6 \text{ \AA}$. The asymptotic (for small r) solution of the two-body problem, $f(r) = \exp[-(2.51/r)^6]$, satisfies these requirements and provides a reasonable starting point for the calculation. We choose

$$f(r) = \exp[-(a_1/r)^{a_2}] \quad (5)$$

as the trial pair function with variable parameters a_1 and a_2 . This function has been used by Wu and Feenberg,¹⁸ The parameter a_1 determines the radius at which the pair function "cuts off" and a_2 determines the sharpness of the cutoff.

We have not yet specified the boundary conditions on the wave function. Since we want to obtain the bulk properties of the liquid, we will eliminate surface effects by imposing periodic boundary conditions on the surface of the cube. This is equivalent to extending the system periodically in space with the periodicity of the

cube. Each particle in the original cubic box [say with coordinates (x, y, z)] will have an image at the same relative position in every other cube [for example at $(x+L, y, z)$]. If we define the distance between particles i and j , r_{ij} , to be the distance from particle i to the nearest image of particle j , the trial wave function is periodic and satisfies the boundary conditions. This choice of boundary conditions is important since we do not wish to take the usual limit $N, \Omega \rightarrow \infty$ with $\rho = N/\Omega$ fixed. We can perform the integrations only for a few particles in a small box so that it is important to eliminate surface effects insofar as this is possible. Since we hope to study the solid as well as the liquid phase, we will choose the particle number N to permit condensation into the cubic-close-packed configuration in the periodic cube; we will use $N = 32$ and 108 .

We have written down the Hamiltonian (1) for the system and a trial wave function (3), (5) containing variational parameters and will be able to perform the calculation for a small number of particles in a periodic box. Our next task is to evaluate the expectation value of the Hamiltonian and to minimize it with respect to the two parameters in the trial wave function. We begin with the ∇_i^2 term in the Hamiltonian¹⁹

$$\int \psi \nabla_i^2 \psi d\tau = \int \psi^2 \sum_{\substack{j \\ (j \neq i)}} \nabla_i^2 \ln f(r_{ij}) d\tau + \int \psi \sum_{\substack{j \\ (j \neq i)}} \nabla_i \ln f(r_{ij}) \cdot \nabla_i \psi d\tau. \quad (6)$$

After integration by parts the second integral is equal to minus one-half of the first. We find easily

$$\int \psi H \psi d\tau = \int \sum_{i < j} \left[-\frac{\hbar^2}{2m} \nabla_i^2 \ln f(r_{ij}) + V(r_{ij}) \right] \psi^2 d\tau. \quad (7)$$

This integral can be written in terms of the two-particle correlation function, defined as

$$g(\mathbf{R}_1 - \mathbf{R}_2) = \rho^{-2} \int \sum_{i \neq j} \delta(\mathbf{R}_1 - \mathbf{r}_i) \times \delta(\mathbf{R}_2 - \mathbf{r}_j) \psi^2 d\tau / \int \psi^2 d\tau. \quad (8)$$

Since the system is translationally invariant, g is a function of $\mathbf{R}_1 - \mathbf{R}_2$ only, and in the liquid state g is spherically symmetric. The correlation function is normalized so that $g(r) = 1$ for large r and

$$\rho \int [g(\mathbf{r}) - 1] d^3r = -1. \quad (9)$$

¹⁶ N. Bogoliubov and D. N. Zubarev, Zh. Eksperim. i Teor. Fiz. 28, 129 (1955) [English transl.: Soviet Phys.—JETP 1, 83 (1955)].

¹⁷ K. Hiroike, Progr. Theoret. Phys. (Kyoto) 27, 342 (1962).

¹⁸ F. Wu and E. Feenberg, Phys. Rev. 122, 739 (1961).

¹⁹ $\int d\tau$ indicates integration of each coordinate \mathbf{r}_i , $i = 1 \cdots N$ over the cubic box.

The liquid structure factor $S(k)$ is related to the correlation function by

$$S(\mathbf{k}) = 1 + \rho \int [g(\mathbf{r}) - 1] e^{i\mathbf{k}\cdot\mathbf{r}} d^3r. \quad (10)$$

The expectation value of H can be written

$$\begin{aligned} & \int \psi H \psi d\tau / \int \psi^2 d\tau \\ & = N\rho/2 \int [-(\hbar^2/2m)\nabla^2 \ln f(r) + V(r)] g(r) d^3r. \end{aligned} \quad (11)$$

We are also interested in the one-particle density matrix defined as

$$\begin{aligned} \rho_1(\mathbf{r}_1 - \mathbf{r}_1') & \equiv N \int \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \\ & \times \psi(\mathbf{r}_1', \mathbf{r}_2, \dots, \mathbf{r}_N) d^3r_2 \dots d^3r_N / \int \psi^2 d\tau. \end{aligned} \quad (12)$$

For small r , $\rho_1(r)$ approaches the density of particles; Penrose and Onsager²⁰ have shown that, for large r , $\rho_1(r)$ approaches the density of particles in the zero-momentum state.

$$\rho_1(r) \rightarrow \rho_0, \quad r \rightarrow \infty. \quad (13)$$

According to Penrose and Onsager it is characteristic of the superfluid phase of the boson system that ρ_0 is some finite fraction of ρ , and these authors estimate that $\rho_0 \approx 0.08\rho$ (8% of the particles are condensed into the zero-momentum state). By Fourier transforming $\rho_1(r)$ we obtain the momentum distribution function

$$n_{\mathbf{k}} = \int [\rho_1(\mathbf{r}) - \rho_0] e^{i\mathbf{k}\cdot\mathbf{r}} d^3r, \quad \mathbf{k} \neq 0. \quad (14)$$

$n_{\mathbf{k}}$ is the average number of particles with momentum \mathbf{k} and is usually written $n_{\mathbf{k}} \equiv \langle N | a_{\mathbf{k}}^\dagger a_{\mathbf{k}} | N \rangle$ where $a_{\mathbf{k}}^\dagger$ and $a_{\mathbf{k}}$ create and destroy particles with momentum \mathbf{k} .

In the weak-coupling theory one calculates $n_{\mathbf{k}}$ and the quantity $m_{\mathbf{k}} \equiv \langle N-1 | a_{\mathbf{k}} a_{-\mathbf{k}} | N+1 \rangle$. We make the Bogoliubov transformation from particle creation and annihilation operators $a_{\mathbf{k}}^\dagger, a_{\mathbf{k}}$ to quasiparticle creation and annihilation operators $\alpha_{\mathbf{k}}^\dagger, \alpha_{\mathbf{k}}$

$$\begin{aligned} a_{\mathbf{k}} &= u_{\mathbf{k}} \alpha_{\mathbf{k}} + v_{\mathbf{k}} \alpha_{-\mathbf{k}}^\dagger, \\ u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2 &= 1, \quad u_{\mathbf{k}} = u_{\mathbf{k}}^* = u_{-\mathbf{k}} \\ v_{\mathbf{k}} &= v_{\mathbf{k}}^* = v_{-\mathbf{k}}, \end{aligned} \quad (15)$$

and assume that the ground state $|0\rangle$ is the state of no quasiparticles

$$\alpha_{\mathbf{k}} |0\rangle = 0. \quad (16)$$

²⁰ O. Penrose and L. Onsager, Phys. Rev. **104**, 576 (1956).

Within this approximation one can easily derive the relation

$$m_{\mathbf{k}}^2 = n_{\mathbf{k}}(n_{\mathbf{k}} + 1). \quad (17)$$

It is of interest to see how well this relation is satisfied for liquid He⁴. We begin with the r -space pairing function

$$\begin{aligned} m(\mathbf{r}_{N-1} - \mathbf{r}_{N+1}) & \equiv N \int \psi_{N-1}(\mathbf{r}_1 \dots \mathbf{r}_{N-1}) \\ & \times \psi_{N+1}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}, \mathbf{r}_N, \mathbf{r}_{N+1}) d^3r_1 \dots d^3r_{N-1}. \end{aligned} \quad (18)$$

With the wave function (3) one can show that

$$m(r) = f(r) \rho_1(r), \quad (19)$$

so that $m(0) = 0$ and $m(r)$ approaches ρ_0 for large r . We obtain $m_{\mathbf{k}}$ by Fourier transforming $m(\mathbf{r})$

$$m_{\mathbf{k}} = \int [m(\mathbf{r}) - \rho_0] e^{i\mathbf{k}\cdot\mathbf{r}} d^3r, \quad \mathbf{k} \neq 0. \quad (20)$$

We now need a numerical technique for determining $g(r)$ and $\rho_1(r)$ from the wave function. $g(r)$ is calculated directly from the probability distribution function P_N [Eq. (4)]. Since the form of P_N is the same as that occurring in the statistical mechanics of the classical gas {replace $f^2(r_{ij})$ by $\exp[-V(r_{ij})/kT]$ }, we can use the same integration techniques that are used in the classical problem. Aviles⁹ has obtained results for the hard-sphere gas at low densities by summing chain diagrams in the Ursell-Mayer cluster development of the integral in powers of the particle density. The cluster expansion limits the validity of the results to very low densities and does not appear to be useful at helium densities.

Metropolis *et al.*²¹ have developed a Monte Carlo method for performing the configuration space integrals of the classical gas when the number of particles is not large. This method consists of performing a biased random walk through configuration space in such a way that this random walk sweeps out the distribution function P_N . One can then estimate the integrals over P_N by averages over the configurations occurring in the random walk. The equation of state of the classical hard-sphere system in the gas and solid phases has been calculated by Wood and Jacobson²² using this Monte Carlo technique for systems of 32 and 108 particles. The results are in good agreement with the calculations of Alder and Wainwright²³ based on an integration of the classical equations of motion for systems of the same size. We have chosen a short-range pair function so that we can use this Monte Carlo method to evaluate the integrals for a small number of particles.

²¹ N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).

²² W. W. Wood and J. D. Jacobson, J. Chem. Phys. **27**, 1207 (1957).

²³ B. J. Alder and T. E. Wainwright, J. Chem. Phys. **27**, 1208 (1957).

MONTE CARLO METHOD

We wish to perform integrations of the form

$$\langle F \rangle = \int F(\mathbf{r}_1 \cdots \mathbf{r}_N) P_N(\mathbf{r}_1 \cdots \mathbf{r}_N) d\tau, \quad (21)$$

where F is symmetric and P_N is a weight function or probability distribution function which is non-negative and normalized to 1 on the $3N$ -dimensional cube.

$$P_N \geq 0, \quad (22)$$

$$\int P_N d\tau = 1.$$

In this application, $P_N(\mathbf{r}_1 \cdots \mathbf{r}_N)$ is the wave function squared and is just the probability of finding particles 1 through N at positions $\mathbf{r}_1 \cdots \mathbf{r}_N$.

We will call a set of positions for each of the N particles a configuration, $R^{(i)} \equiv (\mathbf{r}_1^{(i)} \cdots \mathbf{r}_N^{(i)})$. In order to obtain an estimate of the integral (21) we will sample n configurations, $R^{(i)}$, with the probability distribution $P_N(R^{(i)})$ and average F over the n samples

$$\langle F \rangle \approx \langle F_n \rangle \equiv \frac{1}{n} \sum_{i=1}^n F(R^{(i)}). \quad (23)$$

$\langle F_n \rangle$ approaches $\langle F \rangle$ for large n .

Metropolis *et al.*²¹ have found a method of sampling from P_N which is convenient for a machine computation. These authors set up a biased random walk through configuration space beginning with $R^{(1)}$ which is chosen arbitrarily. A procedure is given for generating $R^{(i+1)}$ from $R^{(i)}$ such that, for a long walk, R recurs with frequency $P_N(R)$, independently of the choice of $R^{(1)}$. $R^{(i+1)}$ is generated from $R^{(i)}$ by moving one particle, say particle j (the particles may be chosen in order or randomly). A trial position $\mathbf{r}_j^{(t)}$ is chosen from a uniform distribution in a cube of volume $(2d)^3$ centered on $\mathbf{r}_j^{(i)}$. That is

$$\begin{aligned} x_j^{(t)} &= x_j^{(i)} + \xi_1 d, \\ y_j^{(t)} &= y_j^{(i)} + \xi_2 d, \\ z_j^{(t)} &= z_j^{(i)} + \xi_3 d, \end{aligned} \quad (24)$$

where ξ_1 , ξ_2 , and ξ_3 are random numbers sampled from a uniform distribution on $-1 < \xi < 1$. We now compute P_N for the old configuration $R^{(i)}$ and for the trial configuration $R^{(t)}$ where

$$R^{(t)} \equiv (\mathbf{r}_1^{(i)}, \dots, \mathbf{r}_{j-1}^{(i)}, \mathbf{r}_j^{(t)}, \mathbf{r}_{j+1}^{(i)}, \dots, \mathbf{r}_N^{(i)}), \quad (25)$$

$R^{(i+1)}$ is taken to be either $R^{(t)}$ or $R^{(i)}$ depending on the values of $P_N(R^{(t)})$ and $P_N(R^{(i)})$.

$$\begin{aligned} R^{(i+1)} &= R^{(t)}; & P_N(R^{(t)}) &\geq P_N(R^{(i)}) \\ &= R^{(i)}; & P_N(R^{(t)}) &< P_N(R^{(i)}) \\ & & & \text{and } P_N(R^{(t)})/P_N(R^{(i)}) > \eta \\ &= R^{(i)}; & P_N(R^{(t)}) &< P_N(R^{(i)}) \\ & & & \text{and } P_N(R^{(t)})/P_N(R^{(i)}) < \eta. \end{aligned} \quad (26)$$

Here η is a random number chosen from a uniform distribution on $0 \leq \eta < 1$. When $P_N(R^{(t)}) > P_N(R^{(i)})$ the system is moving into a region of higher probability and $R^{(t)}$ is accepted as the next configuration. When $P_N(R^{(t)}) < P_N(R^{(i)})$ the system is moving into a region of lower probability and $R^{(t)}$ is accepted only with probability $P_N(R^{(t)})/P_N(R^{(i)})$. The step to $R^{(t)}$ is not made with probability $1 - P_N(R^{(t)})/P_N(R^{(i)})$. This procedure allows free motion of the system into regions of higher probability and inhibits motion into regions of lower probability, forcing the system to spend more time in regions of high probability.

We now demonstrate that this step procedure does choose configurations R with probability $P_N(R)$. Since a particle is allowed to move to any point inside the cube of length $2d$ with finite probability, it is clear that a finite number of moves will allow it to reach any point in the box with finite probability. Since this is true for each particle, any point in configuration space may be reached from any other point with finite probability by a finite number of jumps. Thus the method is ergodic and the random walk will cover all of configuration space.

Next consider a large ensemble of systems and suppose for simplicity that there are a finite number of configurations $R^{(i)}$ with ν_i systems in the i th configuration. We wish to show that after many steps $\nu_i \propto P(R^{(i)})$. Consider a configuration i and a configuration j which can be reached from i in one step and suppose that $P(R^{(i)}) > P(R^{(j)})$. Let p_{ij} be the probability of choosing $R^{(j)}$ as the trial configuration starting from configuration $R^{(i)}$. The step procedure has been set up so that $p_{ij} = p_{ji}$. Then the number of systems in the ensemble moving from i to j in one step is equal to $\nu_i p_{ij} P(R^{(i)})/P(R^{(i)})$, whereas the number of systems moving from j to i is $\nu_j p_{ji}$. At equilibrium these numbers must be equal so that

$$\nu_i/\nu_j = P_N(R^{(i)})/P_N(R^{(j)}) \quad (27)$$

whenever j can be reached from i in one step. Since any configuration can be reached from any other in a finite number of steps, this relation must hold for all i and j . Thus $\nu_i \propto P_N(R^{(i)})$ and this step procedure does generate an equilibrium probability distribution which is equal to P_N . The ergodic property allows us to average over one long walk instead of taking an ensemble average.

In order to use this random walk as a computational device, we must deal with walks with a finite number of steps n . The above demonstration that the average of F over the random walk is equal to the average over P_N (and independent of $R^{(1)}$ which is chosen arbitrarily) holds only as n goes to infinity. In the calculations on the classical hard-sphere gas some difficulty was experienced in achieving equilibrium when the system was very near the gas-solid phase transition. The random walk appeared to remain in one phase for a long time and to jump from one phase to the other only rarely. Wood and Jacobson²² took advantage of this to

calculate the properties of both the gas and solid phases at the same density. We are not able to see this effect in the present calculation and must be satisfied with the equilibrium average over the two phases near the phase transition. In order to assure that the random walks are long enough to provide a good equilibrium average, several of the calculations are performed twice starting from different initial configurations $R^{(1)}$. The two starting configurations are a random configuration with the particles in random positions in the box and an ordered configuration with the particles on the lattice sites of a cubic-close-packed lattice. In all cases the results are independent of the starting configuration within the accuracy of the calculation which indicates that the random walks are long enough to give reliable results. Since the average over the first few steps is obviously dependent on the starting point, these first few configurations are not included in the averaging. We let the system approach equilibrium for $n/2$ steps and take the averages over the next n steps.

The resulting averages are independent of the parameter d provided that the walks are long enough. d is adjusted periodically during the walk to keep the probability of accepting the trial configuration near one-half. This procedure is thought to maximize the rate of motion through configuration space and to aid in the approach to equilibrium.

We now have a procedure for sampling points from configuration space with probability P_N and we want to calculate $g(r)$ and $\rho_1(r)$ from this sample. Computing $g(r)$ for a single configuration is simple. We compute the distance between each pair of particles and count the number of distances which lie between r and $r+dr$. Averaging this number over n configurations gives us an estimate of $(N/2)\rho 4\pi r^2 dr g(r)$. Since only one particle, say particle j , is moved in going from $R^{(i)}$ to $R^{(i+1)}$, the only new information in $R^{(i+1)}$ is the distances r_{jk} , $k \neq j$. Only these distances are used to compute an estimate of $4\pi r^2 dr g(r)$. A typical Monte Carlo estimate for $g(r)$ is shown in Fig. 4 for $N=108$, $\rho=2.2 \times 10^{22}$ atoms/cc, $a_1=2.6$ Å, $a_2=5$. The parameters are those for liquid He⁴ at its equilibrium density.

Since the distance r_{ij} is taken to be the distance between particle i and the nearest image of particle j , we obtain an estimate of $g(r)$ only for $r < L/2$. This distance $L/2$ is 5.6 Å for the 32-particle system and 8.4 Å for the 108-particle system. In computing

$$\langle r^{-n} \rangle \equiv \left\langle \sum_{i < j} r_{ij}^{-n} \right\rangle$$

and $S(k)$ from integrals over $g(r)$, we set $g(r)$ equal to one (the asymptotic value for large r) for $r > L/2$. This introduces a negligible error in $\langle r^{-n} \rangle$ even for the 32-particle system, but it does introduce a truncation error in the Fourier transform integral for $S(k)$. For the parameters mentioned above, the values of $S(k)$ for $k > 0.75$ Å⁻¹ change by less than 0.02 in going from 32

to 108 particles. This change appears to be due primarily to the small maximum in $g(r)$ near $r=7$ Å which is left out of the Fourier transform integral for the 32-particle calculation. For the 108-particle system the values of $S(k)$ are meaningful only for $k > 2\pi/8.4$ Å⁻¹ = 0.75 Å⁻¹.

With the wave function (3) the integral for $\rho_1(r)$ Eq. (12) can be written

$$\rho_1(\mathbf{r}_1 - \mathbf{r}_1') = \frac{\rho}{\Omega} \int \left[\prod_{j>1} f(r_{1j}) / \prod_{j>1} f(r_{1j}') \right] \times P_N(\mathbf{r}_1 \cdots \mathbf{r}_N) d^3r_2 \cdots d^3r_N. \quad (28)$$

We want to compute

$$\rho \prod_{j>1} \frac{f(r_{1j})}{f(r_{1j}')} \quad (29)$$

for the configuration $R^{(i)}$ and average this expression over the configurations in our sample. It is convenient to do the averaging in the following way: We choose N random positions \mathbf{r}_i in the cubic box and compute the distances $r_{i'j}$. We now compute the function

$$F^{(i)}(r) = \sum_{i'j} \prod_{k \neq j} \frac{f(r_{i'k})}{f(r_{jk})}, \quad r < |r_{i'j}| < r + dr, \quad (30)$$

where the sum is taken over all i' and j such that $r_{i'j}$ lies between r and $r+dr$. Averaging this function over configurations gives us an estimate of $\rho_1(r)N4\pi r^2 dr$. The values $F^{(i)}(r)$ and $F^{(i+1)}(r)$ are not independent since only one atom position was changed in going from $R^{(i)}$ to $R^{(i+1)}$. However, $F^{(i)}(r)$ and $F^{(i+N)}(r)$ are roughly independent and we obtain an efficient estimate of $\rho_1(r)$ by averaging over every N th configuration.

$$\rho_1(r) dr = \frac{1}{n4\pi r^2} \sum_{i=1}^{n/N} F^{(iN)}(r). \quad (31)$$

In a large system $\rho_1(r)$ approaches a constant, ρ_0 , for large r . We can obtain an estimate of ρ_0 by noting that the atom positions are uncorrelated over distances greater than $l_c \approx 6$ Å so that $\prod_{j>1} f(r_{1j})$ and $\prod_{j>1} f(r_{1j}')$ are independent for $r_{11'} > 2l_c$. Since the average of the product of two independent quantities is the product of the averages, we have

$$\frac{\rho_0}{\rho} = \int \prod_{j>1} f(r_{1j}) P_N(\mathbf{r}_1 \cdots \mathbf{r}_N) d\tau \times \int \frac{1}{\prod_{j>1} f(r_{1j}')} P_N(\mathbf{r}_1 \cdots \mathbf{r}_N) d\tau. \quad (32)$$

Penrose and Onsager²⁰ used this expression together with the pair function

$$f_{p0}(r) = \begin{cases} 1 & r > 2.6 \text{ Å} \\ 0 & r < 2.6 \text{ Å} \end{cases} \quad (33)$$

to estimate that $\rho_0/\rho \cong 0.08$. A typical estimate of $\rho_1(r)$ and ρ_0 is shown in Fig. 7.

NUMERICAL RESULTS

Preliminary calculations were performed with 32 particles in the box for 41 sets of values for the variational parameters (a_1, a_2). The averaging to obtain $g(r)$ was performed over 4800 configurations. The ground-state energy as a function of a_1 and a_2 for the equilibrium density of liquid He⁴ ($\rho = 2.20 \times 10^{-22}$ atoms/cc) is shown in Fig. 1. The minimum occurs for $a_1 \approx 2.6$ Å and $a_2 \approx 5$. The energy at the minimum is $-0.77 \pm 0.09 \times 10^{-15}$ ergs/atom compared with the experimental ground-state energy of -0.988×10^{-15} ergs/atom. The accuracy of the results for these short runs is not great; in particular, we were not able to see any manifestation of the liquid-solid phase transition.

The next calculations were performed for 32 atoms with averages taken over 32 000 configurations with $a_2 = 5$ and a_1 varied from 2.1 to 3.3 Å in steps of 0.1 Å, again with $\rho = 2.20 \times 10^{22}$ atoms/cc. These 13 runs were made starting with the cubic-close-packed configuration and four of these were repeated starting from the random configuration to make certain that equilibrium had been achieved. No significant differences in $\langle r^{-m} \rangle$ were detected indicating that the Monte Carlo method provided a valid sample of the distribution function.

The "best" values of a_1 for the range of densities occurring in liquid He⁴ fell between 2.6 and 2.8 Å. In order to determine the dependence of the results on the particle number, four runs were made for 108 atoms in the box with $a_1 = 2.6$ and 2.8 Å and starting from the

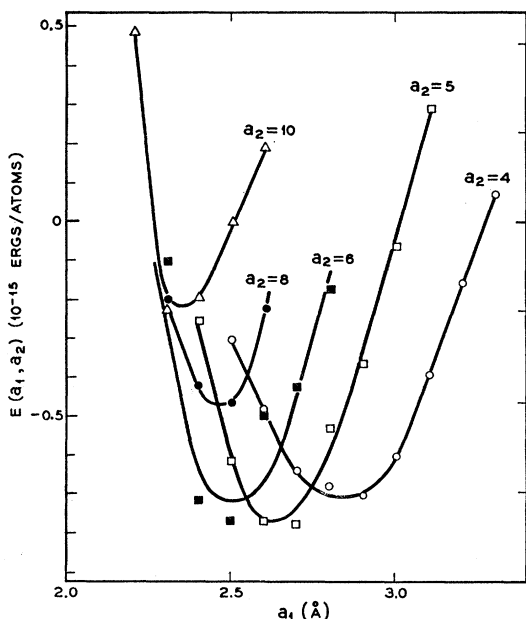


FIG. 1. The ground-state energy versus the two variational parameters, a_1 and a_2 , for the density $\rho = 2.2 \times 10^{-22}$ atoms/cc as found from the preliminary calculations.

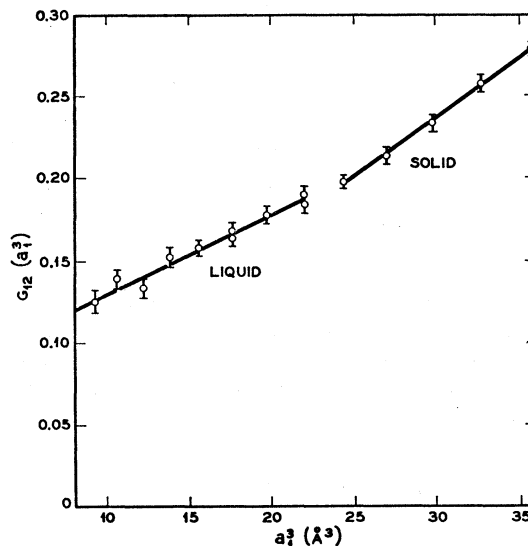


FIG. 2. The function $G_{12}(a_1^3)$ versus a_1^3 from Eq. (34). The points are computed from the values of $\langle r^{-12} \rangle$ from Table I and the error bars indicate the estimated standard deviations. The solid lines show a least-squares fit of a straight line to the numerical data in the two regions.

cubic-close-packed and the random configurations. Again there was no dependence on the initial configuration. It is more striking that no significant differences in $\langle r^{-m} \rangle$ were found between the 32- and 108-particle runs. A difference of 3.3% in $\langle r^{-12} \rangle$ and of 0.9% in $\langle r^{-6} \rangle$ would have been detected by the statistical test used.²⁴ This means that the properties of the 32-particle system approximate the properties of the bulk liquid within a few percent. Values of $\langle r^{-6} \rangle$, $\langle r^{-7} \rangle$, and $\langle r^{-12} \rangle$ (necessary to calculate $\langle H \rangle$) and their standard deviations are listed in Table I.

TABLE I. Numerical values of $\langle r^{-m} \rangle$ in units of Å⁻ⁿ as a function of a_1 for $a_2 = 5$ and $\rho = 2.2 \times 10^{22}$ atoms/cc.

a_1	$R^{(1)}$	N	$10^3 \langle r^{-6} \rangle / N$	$10^8 \langle r^{-7} \rangle / N$	$10^5 \langle r^{-12} \rangle / N$
2.1	fcc	32	4.581 ± 0.033	1.617 ± 0.022	2.019 ± 0.061
2.2	fcc	32	4.253 0.030	1.456 0.014	1.528 0.036
2.3	fcc	32	3.876 0.028	1.278 0.013	1.081 0.029
2.3	random	32	3.869 0.026	1.275 0.012	1.075 0.026
2.4	fcc	32	3.678 0.022	1.184 0.010	0.871 0.022
2.5	fcc	32	3.424 0.016	1.072 0.007	0.676 0.016
2.6	fcc	32	3.234 0.014	0.987 0.006	0.531 0.009
2.6	random	32	3.234 0.015	0.988 0.007	0.542 0.010
2.6	fcc	108	3.240 0.015	0.991 0.007	0.542 0.010
2.6	random	108	3.220 0.016	0.981 0.007	0.525 0.008
2.7	fcc	32	3.068 0.020	0.916 0.008	0.439 0.011
2.7	random	32	3.067 0.013	0.916 0.006	0.438 0.009
2.8	fcc	32	2.920 0.014	0.853 0.006	0.354 0.007
2.8	random	32	2.938 0.013	0.860 0.005	0.363 0.007
2.8	fcc	108	2.942 0.010	0.861 0.005	0.369 0.005
2.8	random	108	2.946 0.012	0.861 0.005	0.365 0.006
2.9	fcc	32	2.795 0.009	0.801 0.004	0.299 0.004
3.0	fcc	32	2.703 0.013	0.763 0.005	0.256 0.005
3.1	fcc	32	2.611 0.011	0.726 0.005	0.224 0.004
3.2	fcc	32	2.543 0.011	0.699 0.004	0.200 0.004
3.3	fcc	32	2.475 0.011	0.672 0.004	0.177 0.004

²⁴ The student t test for significance at the 5% level.

TABLE II. The two parameters of a least-squares fit of $G_m = A_3^{(m)} + A_4^{(m)}a_1^3$ to the data for $\langle r^{-m} \rangle$ in the liquid and solid regions.

m	Liquid		Solid	
	$A_3^{(m)}$	$A_4^{(m)}$	$A_3^{(m)}$	$A_4^{(m)}$
6	$(5.99 \pm 0.09)10^{-2}$	$(9.2 \pm 4.9)10^{-5}$	$(5.83 \pm 0.04)10^{-2}$	$(1.28 \pm 0.13)10^{-4}$
7	$(7.04 \pm 0.14)10^{-2}$	$(6.2 \pm 0.8)10^{-4}$	$(6.85 \pm 0.06)10^{-2}$	$(6.47 \pm 0.21)10^{-4}$
12	$(7.89 \pm 0.54)10^{-2}$	$(5.0 \pm 0.3)10^{-3}$	$(2.52 \pm 0.53)10^{-2}$	$(7.06 \pm 0.19)10^{-3}$

We can now calculate $\langle H \rangle$ as a function of a_1 for a given density and minimize $\langle H \rangle$ with respect to a_1 . Since the values of $\langle r^{-m} \rangle$ contain statistical errors it is convenient to fit these values with an analytic function so that $\langle H \rangle$ can be minimized analytically. The following function is used:

$$\langle r^{-m} \rangle = \frac{2\pi}{5} \rho N a_1^{3-m} 2^{(3-m)/5} \Gamma\left(\frac{m-3}{5}\right) \times [1 + a_1^3 G_m(a_1^3)]. \quad (34)$$

This form for the function is identical to that obtained from the cluster expansion if G_m is expanded in a power series in a_1^3 . The plot of $G_{12}(a_1^3)$ given in Fig. 2 shows a change of slope near $a_1 = 2.85 \text{ \AA}$ and can be fitted by straight line segments on either side of this point. Since other properties of the system show a break in this region, this point is tentatively identified as the liquid-

solid phase transition. The properties which we obtain very near the phase transition represent an averaging of the liquid and solid properties appropriate to the small size of the system. Thus, very near the phase transition, we do not obtain results valid for a large system.

Two terms in the expansion of G_m provided a good fit in the liquid and solid regions separately. The coefficients in this expansion are given in Table II. This analytic form for $\langle r^{-m} \rangle$ can be used to compute the energy and the best value for the parameter a_1 as a function of density in the liquid and solid regions; the results are shown in Fig. 3 and compared with the experimental values.²⁵ The pressure can then be computed from $P = -\partial E / \partial V$ (or by using the virial theorem) and the velocity of sound from $s^2 = \partial P / m \partial \rho$. The theoretical and experimental quantities are compared in Table III for particle densities corresponding to the liquid at zero pressure and the liquid at 25 atm. For the liquid at zero pressure ($\rho = 2.20 \times 10^{22}$ atoms/cc) and $a_2 = 5$ we find $a_1 = 2.60 \pm 0.01 \text{ \AA}$. Figures 4 through 9

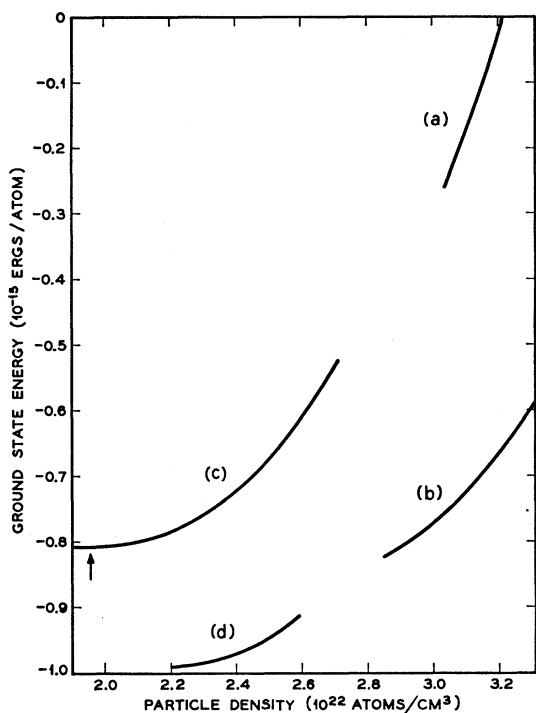


FIG. 3. The experimental and theoretical ground-state energy as a function of particle density for liquid and solid He^4 : (a) solid, theory; (b) solid, experiment; (c) liquid, theory; (d) liquid, experiment. The arrow indicates the minimum of the theoretical curve.

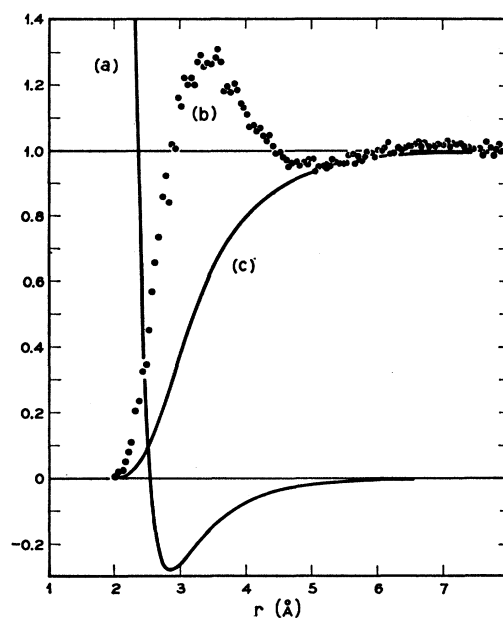


FIG. 4. (a) The two-body potential $V(r)$ in units of 5×10^{-15} ergs. (b) The Monte Carlo estimate of the two-body correlation function $g(r)$ for the equilibrium density of liquid He^4 . (c) The pair function squared $f^2(r)$ for $a_1 = 2.6 \text{ \AA}$, $a_2 = 5$.

²⁵ K. R. Atkins, *Liquid Helium* (Cambridge University Press, Cambridge, 1959).

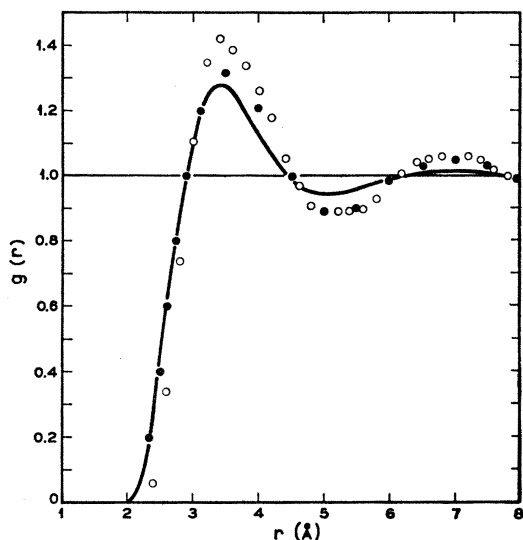


FIG. 5. Comparison of the two-body correlation function with experiment. The solid line is the theoretical curve, the solid circles are computed from the x-ray data of Gordon *et al.* (Ref. 26) and the open circles are computed from the neutron data of Henshaw (Ref. 27).

give the theoretical results for these values of the parameters. In Fig. 4 we show the pair function squared and the Monte Carlo estimate of $g(r)$ for the 108-particle system along with the potential $V(r)$. A smooth curve drawn through these Monte Carlo points for $g(r)$ is shown in Fig. 5 and is compared with the correlation function computed from the x-ray data of Gordon *et al.*²⁶ taken at 1.4°K and the neutron data of Henshaw²⁷ taken at 1.06°K. The liquid structure factor calculated from the Monte Carlo estimate of $g(r)$ using Eq. (10) is shown in Fig. 6 along with the x-ray and neutron data. The Monte Carlo estimate of $\rho_1(r)$ for the 32-particle

TABLE III. Comparison of theory with experiment for the densities of liquid He⁴ at zero pressure and 25 atm.

	Particle density 10 ²² atoms/cc	Theory	Experiment
Minimum energy (10 ⁻¹⁶ erg/atom)		-0.810±0.015	-0.988
Equilibrium density (10 ²² atoms/cc)		1.95±0.02	2.20
Energy (10 ⁻¹⁶ erg/atom)	2.20	-0.781±0.015	-0.988
Energy (10 ⁻¹⁶ erg/atom)	1.59	-0.616±0.025	-0.911
Pressure (atm)	2.20	13 ±2	0
Pressure (atm)	2.59	40 ±6	25
Velocity of sound (m/sec)	2.20	267 ±40	238
Velocity of sound (m/sec)	2.59	316 ±60	365
$\langle V \rangle$ (10 ⁻¹⁶ erg/atom)	2.20	-2.736	
$\langle KE \rangle$ (10 ⁻¹⁶ erg/atom)	2.20	1.955	

²⁶ W. Gordon, C. Shaw, and J. Daunt, *J. Phys. Chem. Solids* **5**, 117 (1958).

²⁷ D. G. Henshaw, *Phys. Rev.* **119**, 9 (1960).

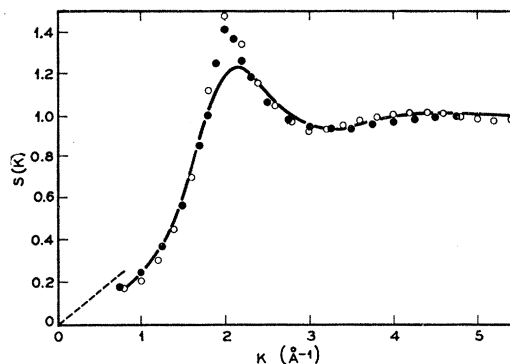


FIG. 6. Comparison of the liquid structure factor with experiment. The solid line is the theoretical curve, the solid circles are from the x-ray data of Gordon *et al.* (Ref. 26), and the open circles are from the neutron data of Henshaw (Ref. 27). The dashed line is computed by the Feynman (Ref. 28) theory from the experimental velocity of sound.

system is shown in Fig. 7; the dashed line gives $\rho_0 = 0.11\rho$ computed from Eq. (32). n_k and m_k , obtained by Fourier transforming $\rho_1(r)$ and $f(r)\rho_1(r)$, are given in Fig. 8.

As seen from Table III and Figs. 3, 5, and 6, the agreement with experiment is reasonably good. The minimum energy is 18% above the experimental value (and is an upper bound on the ground-state energy) and the equilibrium density is 12% less than the experimental density and is in the liquid region. Thus this calculation indicates that the liquid is the stable phase at zero temperature and pressure. However, the location of the liquid-solid phase transition is only tentative and we are not able to calculate the properties of the system very close to the phase transition.

The theoretical correlation function (Fig. 5) agrees well with the experimental one in the position and sharpness of the cutoff near 2.6 Å; the two variational parameters in the pair function adjust the position and sharpness of the cutoff in the pair function. The experimental curves have a higher peak at 3.5 Å and larger oscillations at large r ; this seems to indicate that the pair function should peak up somewhat in the region of greatest attraction, and there was no freedom to do this in the two parameter function which we used.

The structure factor curves of Fig. 6 agree well except in the region of the diffraction maximum at 2 Å⁻¹ where the experimental function is sharply peaked. Neither theory nor experiment provide any information on $S(k)$ for $k < 0.8$ Å⁻¹. The experimental measurements were made above 1°K where $S(k)$ is still strongly temperature-dependent for $k < 0.8$ Å⁻¹. The theoretical curve was obtained by Fourier transforming $[g(r) - 1]$ and truncation errors limit the validity of the $S(k)$ curve to $k > 0.75$ Å⁻¹. For small k the structure factor is expected to approach the Feynman²⁸ value

$$S(k) \sim \hbar k / 2ms, \quad k \rightarrow 0, \quad (35)$$

²⁸ R. P. Feynman, *Phys. Rev.* **94**, 262 (1954).

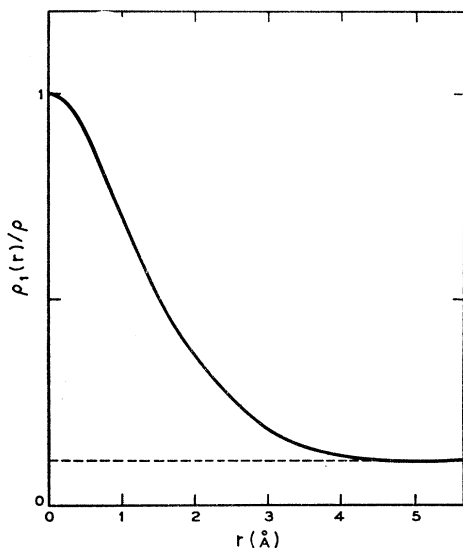


FIG. 7. The single-particle density matrix as a function of separation. The dashed curve indicates the asymptotic limit for large r , $\rho_1(r) \sim \rho_0 = 0.11\rho$.

where s is the velocity of sound. This limit is given by the dashed line in Fig. 6. There is no reason to expect that the theoretical $S(k)$, calculated from the short-range pair function of Eq. (5), will go to zero linearly with k . If one extrapolates the present results to large N , it appears that $S(k)$ approaches a constant ≈ 0.05 to 0.1 as k goes to zero. In the low-density theory the pair function varies as $(1 - a/r^2)$ for large r and one obtains the Feynman form for $S(k)$. By restricting ourselves to a short-range pair function, we obtain qualitatively incorrect results for small k .

The one-particle density matrix (Fig. 7) approaches an asymptotic value, $\rho_0/\rho = 0.11 \pm 0.01$, at a rather small distance $\approx 4 \text{ \AA}$. The fact that the density matrix approaches a nonzero limit for large r indicates, according to the criterion of Penrose and Onsager, that the system is in the condensed or superfluid phase. The momentum distribution (n_k in Fig. 8) approaches a constant, ≈ 0.75 atoms/momentum state, for small k , is approximately Gaussian for $k < 2 \text{ \AA}^{-1}$, but has a roughly constant shoulder extending from 2 to 3 \AA^{-1} . This shoulder is emphasized by plotting $k^2 n_k$ (Fig. 9) which is proportional to the number of atoms with momentum of magnitude k . This function exhibits two peaks with a minimum near 2 \AA^{-1} . Fifteen percent of the atoms are in the peak at $k = 2.5 \text{ \AA}^{-1}$ and these atoms carry 45% of the kinetic energy. In the low-density model n_k is proportional to k^{-1} for small k , and Onsager²⁹ has suggested that this form is model-independent. In the present calculation we find that n_k approaches a constant for small k and we again obtain qualitatively incorrect results for small k . We can estimate the errors involved here by fitting the k^{-1} dependence for small k (the dashed curve

²⁹ L. Onsager (private communication).

in Fig. 9) smoothly onto the computed n_k curve. The area between the dashed and solid curves of Fig. 9 contains about 3% of the atoms and this introduces a possible error of 3% into ρ_0 but does not affect the kinetic energy.

The pair function, m_k (Fig. 8), approaches -0.066 for small k , passes through zero at 2 \AA^{-1} , and is roughly equal to n_k for large k . m_k should also be proportional to k^{-1} for small k and this form is given by the dashed curve of Fig. 9. For $k=0$ we have $n_0 = m_0 = 0.11N \gg 1$ so that the relation $m_k^2 = n_k(n_k + 1)$ holds. For $k \neq 0$, m_k is about a factor of 10 too small for this relation to hold.

DISCUSSION

Two qualitative conclusions have emerged from the calculation: (1) that He^4 is a liquid at zero temperature and pressure, and (2) that liquid He^4 is a condensed phase corresponding to a generalized Bose-Einstein condensation with about 10% of the atoms in a single-quantum state. We have found reasonably good agreement with the experimental information on the ground-state energy as a function of density and the two-particle correlation function. We would like to examine the various approximations which have been made during the course of the calculation which affect its range of validity. We have written down a Hamiltonian (1) for spinless bosons interacting through a two-body potential; this is probably a good approximation for the experimental range of densities of liquid and solid helium. One might hope to improve upon the particular two-body potential that we have chosen and, in fact, the ground-state calculation may prove to be a sensitive testing ground for helium potentials. The ansatz (3) for the ground-state wave function is correct for the weakly interacting or low-density gas and provides quantitative

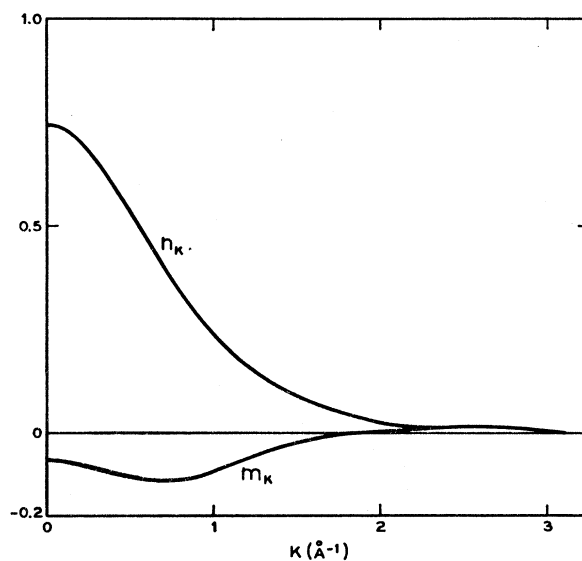


FIG. 8. The momentum distribution function n_k and the pairing function m_k as a function of wave number.

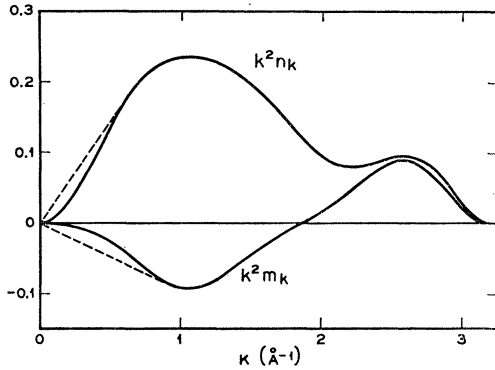


FIG. 9. The momentum distribution function and the pairing function multiplied by k^2 to emphasize the behavior at large k . The dashed lines show the expected asymptotic form for small k .

results for liquid helium; it may also prove to be useful for solid helium which is difficult to treat by the usual techniques. By choosing a form for the pair function which will allow it to take better advantage of the attractive part of the potential, we should be able to get significantly better agreement with the ground-state energy. The restriction that the pair function be short ranged probably does not affect the energy very much but does affect the small k behavior of $S(k)$ and n_k . It would be interesting to find a technique for handling a weak, long-ranged part of the pair function in

addition to the strongly correlated part at short distances where the potential is strong.

The restriction to a small number of particles seriously limits the range of validity of the calculation. It is reasonable to expect good results provided that the length L of the periodic cube is much larger than a correlation length l_c , the distance over which the motions of two particles are appreciably correlated. Since the important correlations in liquid He⁴ occur over distances of the order of the interparticle spacing, l_c is much less than L for the particle numbers we have considered. However, there may be errors near the liquid-solid phase transition and we have not attempted to estimate the errors involved in the solid region. In the low-density Bose gas the correlation length is much larger than the interparticle spacing and we would not get good results with a few particles. The statistical accuracy of the Monte Carlo method is limited but it is sufficient for the present purpose; the standard deviation of the ground-state energy is 2%.

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