PHYSICAL REVIEW VOLUME 164, NUMBER 1 5 DECEMBER 1967

Variational Calculations on Liquid He^4 and He^3†

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(Received 13 July 1967)

Assuming a Lennard-Jones 6-12 potential with the de Boer–Michels parameters, the ground-state energies of systems of liquid He^4 and He^3 are calculated by a variational procedure in conjunction with the method of correlated basis functions. Comparisons are made with the results of McMillan and of Schiff and Verlet. These comparisons shed some light on the validity and adequacy of the Jastrow- and Jastrow-Slater–type wave functions in the description of helium liquids.

THE ground states of liquid He^4 and He^3 have been the subject of many theoretical studies. The more realistic calculations for liquid He^4 and the hypothetical boson He^3 system are frequently variational, whereas the treatment of liquid He^3 requires more elaborate procedures. Recent work[1] has shown that a perturbation theory based on the method of correlated basis functions (CBF) can start from a variational calculation and lead to encouraging results for the ground state of liquid He^3. In earlier papers[1,2] we reported on calculations of the ground-state properties of liquid He^4 and He^3 using variational methods in conjunction with CBF. In those calculations we used a two-body Lennard-Jones potential $v(r)$, with the strength and range parameters ϵ and σ determined by Massey[2] in a self-consistent manner which forced the calculations to give the correct ground-state energy and equilibrium density for liquid He^4. In this paper we give the results of a new calculation using the de Boer–Michels values for ϵ and σ. This new calculation enables us to compare our results with those of other authors. In turn, such a comparison sheds some light on the validity and accuracy of the approximations used in these various calculations.

We first discuss the variational calculations for boson systems. The Hamiltonian of such a system is given by

$$H=\sum_{i=1}^{N}\frac{-\hbar^2}{2m}\nabla_i^2+\sum_{i<j;\,i=1}^{N}v(r_{ij})\,, \tag{1}$$

$$v(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]. \tag{2}$$

We choose for ϵ and σ the values determined by de Boer and Michels: $\epsilon=10.22°\mathrm{K}$ and $\sigma=2.556$ Å. A Jastrow-type trial wave function is assumed:

$$\psi_0{}^B(\mathbf{r}_1,\cdots,\mathbf{r}_N)=\exp\{\tfrac{1}{2}\sum_{i<j;\,i=1}^{N}u(r_{ij})\}. \tag{3}$$

The expectation value $\langle H\rangle$ of the energy is then given by

$$\begin{aligned}\langle H\rangle&=\langle T\rangle+\langle V\rangle\,,\\ \langle T\rangle&=N\rho\frac{\hbar^2}{8M}\int g'(r)u'(r)d\mathbf{r}\,,\\ \langle V\rangle&=N\rho\frac{1}{2}\int g(r)v(r)d\mathbf{r}\,,\end{aligned} \tag{4}$$

where ρ is the number density and $g(r)$ is the radial distribution function defined by

$$\begin{aligned}\rho^2g(r)&=N(N-1)\int|\psi_0{}^B|^2d\mathbf{r}_3\cdots d\mathbf{r}_N/I\,,\\ I&=\int|\psi_0{}^B|^2d\mathbf{r}_1\cdots d\mathbf{r}_N.\end{aligned} \tag{5}$$

The evaluation of $\langle H\rangle$ can be carried out by methods of two general categories. In the first case one assumes a parametrized form of $u(r)$ and evaluates approximately the many-body integral for $g(r)$ directly from its definition, according to Eqs. (5) and (3). McMillan[3] (M) performed a Monte-Carlo integration to obtain $g(r)$ in this manner, while Schiff and Verlet[4] (SV) took advantage of the mathematical analogy with the classical theory of fluids and applied the technique of molecular dynamics. Our work (MW) belongs to the second category in which one uses an approximate integro-differential equation to relate $g(r)$ to $u(r)$. Depending upon the approximation chosen, this equation can take on one of several forms. We choose the BBGKY equation in which the three-particle distribution function

$$p^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=N(N-1)(N-2)\int|\psi_0{}^B|^2d\mathbf{r}_4\cdots d\mathbf{r}_N/I$$

is approximated by the Kirkwood superposition form

$$p^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\rho^3g(r_{12})g(r_{23})g(r_{13}).$$

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† This research was supported by the U. S. Atomic Energy Commission.

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TABLE I. Comparison of $\langle T\rangle$, $\langle V\rangle$, and $\langle E\rangle$, in units of °K/N, for He^4 at two densities.

ρ/ρ_0	Authors	$\langle T\rangle$	$\langle V\rangle$	$\langle H\rangle$
	McMillan	11.7	−17.6	−5.9
0.9	Schiff and Verlet	11.59	−17.55	−5.96
	Massey and Woo	11.60	−17.15	−5.55
	McMillan	14.16	−19.82	−5.66
1.0	Schiff and Verlet	13.73	−19.46	−5.73
	Massey and Woo	14.30	−20.32	−6.02

The equation appears as

$$u'(r)=g'(r)/g(r)-\rho\int g(r')u(r')\times[g(|\mathbf{r}-\mathbf{r}'|)-1]\cos(\mathbf{r},\mathbf{r}')d\mathbf{r}'. \tag{6}$$

Our calculation further differs from those of the first category in that we start out with a parametrized form for $g(r)$ instead of $u(r)$. The $g(r)$ chosen has the following form:

$$g(r)=(c+1)e^{-(d/r)^{10}}-ce^{-(1+z)(d/r)^{10}}+A\left\{\left(\frac{d}{r}\right)^6e^{-(1+y)(d/r)^{10}}-B\left(\frac{d}{r}\right)^8e^{-(1+q)(d/r)^{10}}\right\}, \tag{7}$$

$$d^3=\eta/2\pi\rho,$$

$$c=[(1.155574/\eta)-1/1-(1+z)^{0.3}],$$

$$B=\Gamma(0.3)(1+q)^{0.5}/\Gamma(0.5)(1+y)^{0.3},$$

where η, z, A, y, and q are all variational parameters. $u(r)$ is obtained by solving Eq. (6) numerically. The reasons for choosing this form of $g(r)$ and details concerning our method of calculation are given in an earlier paper.[2]

The trial wave functions chosen by M and SV are much simpler in form:

$$u(r)=-c/r^m. \tag{8}$$

Both M and SV found m to be about 5 over a large range of densities.

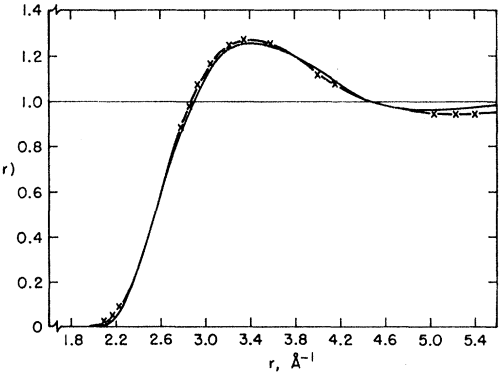

FIG. 1. Comparison of $g(r)$ for He^4 at $\rho\simeq\rho_0=0.0218$ atoms/Å^3. Solid curve MW; solid curve with crosses SV.

TABLE II. Comparison of equilibrium density and energy (°K/N).

Authors	ρ_{eq}/ρ_0	$\langle H\rangle$
McMillian	0.89±0.01	−5.9 ±0.1
Schiff and Verlet	0.9 ±0.1	−5.95±0.2
Massey and Woo	1.05±0.01	−6.06±0.02
Experiment	1.0	−7.14

Figure 1 shows $g(r)$ calculated by SV and MW at $\rho\simeq\rho_0=0.0218$ atoms/Å^3. The two curves are in very good agreement. The disagreement at small r, 1.9 Å$<r<$2.2 Å, is a consequence of the different forms chosen for the trial functions. Note that[2]

$$\lim_{r\to0}u(r)\sim\ln g(r). \tag{9}$$

Thus,

$$\lim_{r\to0}g_{\text{MW}}(r)\sim e^{-(d/r)^{10}},\qquad \lim_{r\to0}u_{\text{MW}}(r)\sim b/r^{10}; \tag{10}$$

whereas for SV one has

$$\lim_{r\to0}u_{\text{SV}}(r)\sim-c/r^5,$$

and

$$\lim_{r\to0}g_{\text{SV}}(r)\sim e^{c/r^5}. \tag{11}$$

This disagreement for small values of r shows up clearly in Fig. 2 where $u(r)$ obtained by M, SV, and MW are compared (at $\rho\simeq\rho_0$). The r^{-5} dependence of the M and SV correlation functions is in agreement with the solution of the two-body equation near r equal to zero.[5]

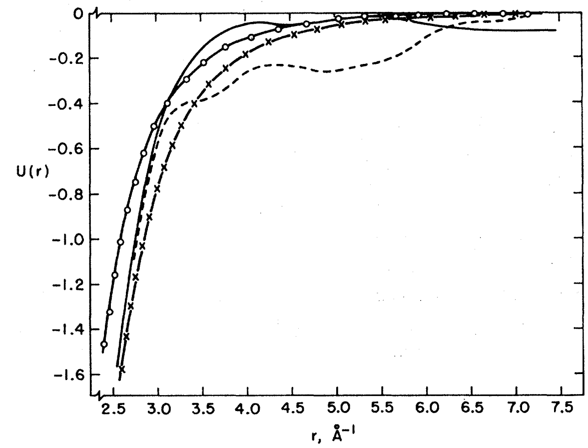

FIG. 2. Comparison of $u(r)$ at $\rho\simeq\rho_0$. Solid curve MW; solid curve with crosses SV; solid curve with open circles M; dashed curve, Wu [F. Y. Wu and E. Feenberg, Phys. Rev. **122**, 739 (1961)], solution of the BBGKY equation using the experimental $g(r)$ of Goldstein and Reekie.

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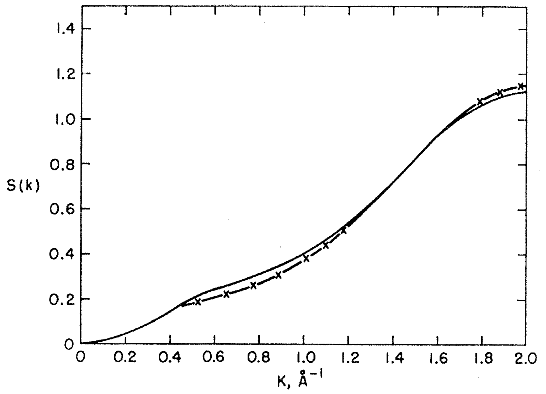

FIG. 3. Comparison of $S(k)$ for the boson He^3 system at $\rho=0.75$, $\rho_0=0.0164$ atoms/Å^3. Solid curve MW; solid curve with crosses SV.

The somewhat longer range of our $u(r)$ is inconsequential: This is evident from the quick approach of $g(r)$ toward unity, and has also been verified by our test calculations which compare $\langle T\rangle$ evaluated with different long-range cutoffs. The further discrepancy between the $u(r)$, s at intermediate values of r probably results from the fact that $u(r)$ depends more sensitively on the variational parameters than does $g(r)$. (See Ref. 2, Figs. 6 and 9.) The energy expectation values obtained are compared in Tables I and II. Table I exhibits the comparison at two densities, $\rho \lesssim \rho_0$. Since the cancellation between $\langle T\rangle$ and $\langle V\rangle$ is strong, the comparison of numerical results becomes very delicate. It is difficult to compare our results at high densities with those of SV, whose $\langle T\rangle$ and $\langle V\rangle$ when plotted against density exhibit large fluctuations. Table II compares our minimum energy and equilibrium density with those of M and SV and with experiment. On the whole, the results of the various calculations are in strikingly good agreement. They share a common deficit of about 1°K/N in comparison with the binding energy found experimentally. This suggests that further investigations should be directed toward our common assumptions: (1) the Jastrow trial wave function, and (2) the de Boer–Michels potential. On one hand, the inclusion of higher-order correlations in the trial wave function may decrease the discrepancy between theory and experiment. On the other hand, we should point out the very sensitive dependence of $\langle H\rangle$ on $v(r)$. In our earlier work,[2] it was shown that the experimental energy could be obtained with a mere 3% shift of the de Boer–Michels potential well toward larger r, without changing the strength of the interaction. Also, using the potential determined by Haberlandt, SV obtained an energy which is actually lower than the experimental value.

TABLE III. Comparison of boson He^3 results (energies in °K/N).

Authors	ρ/ρ_0	$\langle T\rangle$	$\langle V\rangle$	$\langle H\rangle$
Schiff and Verlet	0.65	8.68	−11.60	−2.92
Massey and Woo	0.64	9.98	−12.04	−2.06
	0.72	11.52	−13.63	−2.11

TABLE IV. Comparison of He^3 results (energies in °K/N).

	ρ_{eq}/ρ_0	$\langle H\rangle$	E_1^F	E_2^F	E_3^F	$E^{(0)}$
Schiff and Verlet	0.65	−2.92	2.71	−0.94	−0.12	−1.27
Massey and Woo	0.64	−2.063	2.686	−0.699	−0.125	−0.200
Experiment	0.75					−2.52

Table III gives results on the hypothetical boson He^3 system. Rows 1 and 3 show results at the calculated equilibrium densities. As evidenced by the comparison of row 2 with row 1, the major discrepancy between MW and SV lies in the evaluation of $\langle T\rangle$. There are two obvious sources of inadequacy in our calculation: the Kirkwood superposition approximation for $p^{(3)}$ and the incorrect behavior of $u(r)$ in the limit of small r. Both affect $\langle T\rangle$ directly. Since $\langle V\rangle$ explicitly depends only on $g(r)$, it is clear that neither inadequacy should affect $\langle V\rangle$ in first order. It should be possible to estimate separately the effects of these two approximations: Our calculation is now being extended to incorporate in $u(r)$ all the expected features; this will then isolate the error due to the remaining superposition approximation. On account of the difference in $\langle T\rangle$, the total energies $\langle H\rangle$ of SV and MW are quite different. This difference enters directly into the fermion calculations, as will be seen below.

The variational calculation for liquid He^3 begins with the trial wave function $\psi_0{}^B\Phi_0$, where $\psi_0{}^B$ is taken from the above boson He^3 calculation and assumed to be exact, and Φ_0 is a Slater determinant of plane waves and spin functions, with momenta filling a pair of Fermi spheres of opposite spins. The energy expectation value $E^{(0)}$ is obtained with the aid of a cluster expansion, resulting in the series

$$
\begin{aligned}
E^{(0)} &= \langle H\rangle + E_1{}^F + E_2{}^F + E_3{}^F + \cdots, \\
E_1{}^F &= \tfrac{3}{5} N e_F, \\
E_2{}^F &= 24 N e_F \int_0^1 [S(2k_F x)-1][1-\tfrac{3}{2}x+\tfrac{1}{2}x^3] x^4 dx, \\
E_3{}^F &= -\left(\frac{3}{8\pi}\right)^3 N e_F \int_{\text{unit sphere}} x_{12}{}^2 S(k_F x_{12}) \\
&\qquad \times [S(k_F x_{23})-1][S(k_F x_{31})-1] d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_3, \qquad (12) \\
e_F &= \hbar^2 k_F{}^2/2m, \\
k_F{}^3 &= 3\pi^2 \rho, \\
S(k) &= 1+\rho \int e^{i\mathbf{k}\cdot\mathbf{r}} [g(r)-1] d\mathbf{r},
\end{aligned}
$$

and $\langle H\rangle$ is the energy expectation value calculated above for the hypothetical boson He^3 system. Figure 3 shows $S(k)$ obtained by SV and MW at $\rho=0.75\rho_0$, the experimental equilibrium density. Again the agreement is excellent. Table IV compares the calculated equilibrium results. Actually SV varied their $\psi_0{}^B$ in this calculation and obtain $E^{(0)}=-1.35°\mathrm{K}/N$. What we have quoted in Table IV are the results they would have obtained had they used our approximation that $\psi_0{}^B$ is the *exact* solution of the boson He^3 problem. This approximation is seen to be very good. Note the dominating effect of $\langle H\rangle$ on $E^{(0)}$. Note also in our calculation that as the Fermi statistics gets "turned on," the equilibrium density drops (from $0.72\rho_0$ to $0.64\rho_0$), an obvious consequence of the Pauli repulsion.

In Ref. 1 we worked out an extension of this variational calculation to include a perturbation correction in second order. The correction depends solely on ρ and $S(k)$, and amounts to $-0.33°\mathrm{K}/N$. Since the SV calculation offers ρ_0 and $S(k)$ very similar to those obtained by us, we expect the second-order correction to their variational energy to be of roughly the same magnitude. In other words, starting with their $\psi_0{}^B$, we can construct a correlated basis and obtain a perturbed energy of roughly $-1.7°\mathrm{K}/N$, in much better agreement with experiment than all previous calculations. The remaining discrepancy of about $0.8°\mathrm{K}/N$ may again be a consequence of the absence of higher-order correlations in the trial function and the uncertainty in the two-body potential $v(r)$.

PHYSICAL REVIEW VOLUME 164, NUMBER 1 5 DECEMBER 1967

Order of the He^4 II–He^4 I Transition under Rotation

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(Received 16 June 1967)

Purely thermodynamic considerations show that the volume discontinuity at the He^4 II → He^4 I transition under rotation reported by Andronikashvili and Tsakadze cannot correspond to a transition between thermodynamic equilibrium states if $(\partial P/\partial T_\lambda)_\omega<0$. Experimental results are presented which show that at the transition $|\Delta H|\leqslant 6\times10^{-4}$ J/mole and $|\Delta V|\leqslant 3\times10^{-5}$ cc/mole at $\omega=30$ sec^{-1}. Thus, within these limits, the transition is of higher than first order.

INTRODUCTION

PYCNOMETRIC measurements for rotating He^4 II reported by Andronikashvili and Tsakadze (AT)[1] showed that the molar volume $V(He^4\,\mathrm{II})$ decreases with increasing angular velocity ω. In somewhat later communications,[2] AT presented measurements which indicated that $V(He^4\,\mathrm{I})$ is independent of ω, and that at $\omega>0$, the molar volume is discontinuous at the transition temperature T_λ. Very recent attempts by Smith *et al.*,[3] and by Andelin[4] to reproduce AT's results below the transition temperature by slightly different techniques were unsuccessful. In a brief previous communication[5] this author reported on thermal measurements which revealed no dependence of the entropy of He^4 II on angular velocity.

No quantitative conclusions can be drawn regarding the dependence of the internal energy of He^4 II upon ω from AT's earlier measurements.[1] However, at the transition the Clausius-Clapeyron relation yields a large entropy discontinuity from AT's latter measurements. Therefore, the absence or presence of the reported first-order contribution to the transition is particularly important, because the corresponding entropy discontinuity indicates a dependence of the internal energy of He^4 II, immediately below the transition, upon ω which exceeds the angular momentum contribution expected for solid-body rotation by three orders of magnitude.

Note added in proof. Very recently Pobell *et al.* [Phys. Letters **25A**, 209 (1967)] reported on measurements somewhat similar to those reported here. However, they attempted to relate changes in entropy with ω to changes in volume with ω at temperatures *well below* T_λ. Therefore, it seems worthwhile to emphasize that with available experimental information,[1,2] this is possible only in the *immediate vicinity* of T_λ. The conclusion that $\Delta\rho/\rho\lesssim 2\times10^{-6}$ for the measurements of Pobell *et al.* at 1.80°K and $\omega=110$ sec^{-1}, which is based on thermal measurements, is thus not justified.

It is the purpose of this paper to present the results of thermal measurement, particularly in the immediate

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