PHYSICAL REVIEW A VOLUME 5, NUMBER 1 JANUARY 1972

Use of Ground-State Energy Calculations in Determining the Helium-Helium Interaction*

R. D. Murphy
IBM Research Laboratory, San Jose, California 95114
and Department of Physics, Memorial University of Newfoundland,
St. John's, Newfoundland, Canada†

(Received 12 August 1971)

A variational Monte Carlo calculation of the ground-state energy of liquid He^4 has been performed with a product wave function of a flexible analytic form using several different proposed pair potentials. The calculated ground-state energy, particularly its density dependence, depends sensitively on the form of the pair interaction potential used. The variational nature of the calculations is used to set limits on the depth of some of the proposed forms of the pair potential.

I. INTRODUCTION

Several recent variational calculations[1-4] of the ground-state energy of liquid He^4 have been made by assuming that the ground-state wave function could be written as a product of pair functions and then evaluating the ground-state energy by various means. In this paper we will present the results of a variational Monte Carlo calculation which because of the use of a more general analytic form of the wave function than previously[2-4] used gives better results for the radial distribution function and ground-state energy. The calculations have been made for a number of different proposed forms of the two-body interaction potential and we have found, as before,[4,5] that the results, particularly the density dependence of the energy, are sensitive to the form of the two-body interaction used.

One method of constructing a semiempirical two-body potential is, roughly speaking, to use theoretical calculations (leading generally to an exponential dependence on r, the interparticle separation) for the steep repulsion at small r, plus the correct asymptotic dependence, i.e., $-C_6/r^6-C_8/r^8$, for large r, and to interpolate between these two limits by fitting the potential in the region near the minimum with a function containing one or more adjustable parameters to be determined from the second virial coefficient, gas transport data, etc. Barker and co-workers[6,7] have by this method determined a very useful potential for Ar with an uncertainty of about 1%. Beck[8] and Bruch and McGee[9,10] have made systematic investigations using similar techniques for the case of helium, which is more complicated because of the dominant role of quantum effects. For example, although the depth of the potential well and the location of the minimum, which cannot be determined very precisely from virial coefficient and transport data, could in principle be determined quite accurately for a classical substance by requiring the potential to yield the correct cohesive energy and lattice parameter of the solid at 0 °K in a quasiharmonic theory, this procedure is quite inapplicable to a quantum solid such as helium. It is not surprising, therefore, that Bruch and McGee quote an uncertainty of about ± 5% in the well depth and ± 1% in the location of the minimum in their potentials. We find that the present calculations of the ground state of liquid He^4, because of their strict variational nature, can be used to reduce the uncertainty in the Bruch-McGee potentials by setting limits on the well depth as a function of the location of the minimum.

In the present work, we have considered for simplicity only the Lennard-Jones (LJ), Beck, and Bruch-McGee potentials since they are defined by analytic expressions for all values of the interparticle separation.

II. FORMULATION

The Hamiltonian H for a system of N He^4 particles in volume V is

$$H=\sum_{i=1}^{N}\frac{-\hbar^2}{2m}\nabla_i^2+U , \tag{1}$$

where U is the potential energy. It may be written as

$$U=U_2+U_3+\cdots , \tag{2}$$

where

$$U_2=\sum_{i<j}u_2(i,j) , \tag{3}$$

$$U_3=\sum_{i<j<k}u_3(i,j,k) , \qquad \text{etc.}, \tag{4}$$

and the quantities $u_n(i,j,k,\ldots)$ represent the nonadditive interactions of n particles, so that all of the u_n approach zero if any of the n particles is far from the other $n-1$ particles.

The two-body potential is frequently taken to be u_{LJ}, the LJ potential:

$$u_{\mathrm{LJ}}(i,j) = 4\epsilon_{\mathrm{LJ}}[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}] \ , \qquad (5)$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$, $\epsilon_{\mathrm{LJ}}/k = 10.22\ ^\circ\mathrm{K}$, and $\sigma = 2.556$ Å. Although our calculations have been done for a number of different proposed forms of u_2, we have found it convenient to measure energies in units of ϵ_{LJ} and distances in units of σ.

We have assumed that all u_n are negligible for $n > 3$ and that the only important term in u_3 is the long-range triple-dipole dispersion interaction, which is

$$u_3(i,j,k) = \frac{\nu(1 + 3\cos\theta_1\cos\theta_2\cos\theta_3)}{r_{ij}^{\ 3}\, r_{jk}^{\ 3}\, r_{ik}^{\ 3}} \ , \qquad (6)$$

where the angles θ_i are the interior angles of the triangle formed by the particles at positions $\vec{r}_i$, $\vec{r}_j$, $\vec{r}_k$, and the coefficient ν is given by Leonard's value[11] of 2.1005×10^{-85} erg cm^9.

If a trial wave function of the form

$$\psi = \prod_{i<j} f(r_{ij}) = \exp\Big[-\tfrac{1}{2}\sum_{i<j} w(r_{ij})\Big] \qquad (7)$$

is assumed, then E_0, the ground-state expectation value of the Hamiltonian, is given by

$$\begin{aligned} E_0 &= \int \psi H \psi d^{3N} r \Big/ \int \psi^2 d^{3N} r \\ &= \tfrac{1}{2} N\rho \int g_2(r)[u_2(r) + (\hbar^2/4m)\nabla^2 w(r)] d^3 r \\ &\quad + \tfrac{1}{6} N\rho^2 \int g_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) u_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) d^3 r_2 d^3 r_3 \ , \qquad (8) \end{aligned}$$

where

$$g_2(|\vec{r}_1 - \vec{r}_2|) = N(N-1)\rho^{-2} \int \psi^2 d^3 r_3 \cdots d^3 r_N \Big/ \int \psi^2 d^3 r_1 \cdots d^3 r_N \ ,$$

$$g_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) = N(N-1)(N-2)\rho^{-3} \int \psi^2 d^3 r_4 \cdots d^3 r_N \Big/ \int \psi^2 d^3 r_1 \cdots d^3 r_N \ ,$$

and $\rho = N/V$ is the particle density. The quantities g_2 and g_3 are the two- and three-particle distribution functions; they are readily seen to be equal to the two- and three-particle distribution functions of the fictitious classical gas at density ρ and temperature T^* interacting via a pair potential $kT^* w(r)$. We evaluated $g_2(r)$ by the "biased random walk" Monte Carlo method familiar from classical statistical mechanics. We considered a system of 32 particles with periodic boundary conditions, and averaged over the last 352 000 configurations. Although this leads to a statistical error of about 2 or 3% in any individual Monte Carlo run, we used a fine mesh in the variational parameter and smoothed the results, leading to an estimated uncertainty in our results of less than 0.5%.

For $\langle U_3 \rangle$, we relied on a previous calculation[12] of the contribution of the triple-dipole term to the binding energy of liquid helium. The result is, to a very good approximation,

$$\langle U_3 \rangle \simeq 0.014 N \epsilon_{\mathrm{LJ}} (\rho/\rho_0)^3 \simeq 0.14 N (\rho/\rho_0)^3\ ^\circ\mathrm{K} \ , \qquad (9)$$

where $\rho_0 \sigma^3 = 0.364$ is the equilibrium density of liquid He^4. The three-body forces are very small, constituting only about 2% of the binding energy of liquid He^4 at the equilibrium density. Although we believe that $\langle U_3 \rangle$ is essentially independent of the wave function used, in fact the liquid results were evaluated for the same form of $w(r)$ used in the present work. Since they are small and essentially independent of α, we have simply added them in as a perturbation, a procedure which should be satisfactory for most calculations. The effect of the three-body terms is to raise the energies slightly and lower the calculated equilibrium densities slightly.

III. RESULTS

Previous calculations[2–4] have used the functional form $w(r) = (\alpha/r)^5$, with α a variational parameter that minimized the energy at a value of 1.17σ. One of the essential features of this choice of $w(r)$ is that the resulting radial distribution function has a scaling property, namely, $g_2(\rho, \alpha, r) = g_2(\rho\alpha^3, r/\alpha)$, that permits one to reuse at any density calculations made for a range of α at a single density (in our calculation the equilibrium density) and thereby obtain the density dependence of the energy. We used in the present calculation a more flexible form for $w(r)$ that retains this scaling property, namely, $w(r) = (\alpha/r)^m \pm (\alpha/r)^n$, with α again a variational parameter. The exponents m and n were used as variational parameters, but they were restricted to be integers with $m > n > 3$. The choice that leads to the lowest energy for all potentials considered and best agreement with the experimental $g(r)$ is $w(r) = (\alpha/r)^5 + (\alpha/r)^4$, although the choice $(\alpha/r)^6 + (\alpha/r)^4$ is very nearly as good. The minimum of the energy occurred for $\alpha/\sigma = 1.07 \pm 0.02$, depending, as did previous calculations,[4] on the potential.

It is most interesting that the best forms of $w(r)$ were a sum of two positive terms (corresponding to a classical fluid interacting via a purely repulsive potential) rather than a sum of one positive and one negative term (corresponding to a classical fluid with a short-range repulsion and long-range attraction) as one might have expected. The explanation lies in the fact that in the former case $f(r)$ increases monotonically to unity rather than having a maximum and decreasing monotonically to unity as it does in the latter case; forms having such a maximum, however, have greater curvature and hence higher kinetic energy and are thus less suitable for this variational calculation. The same remarks apply to forms

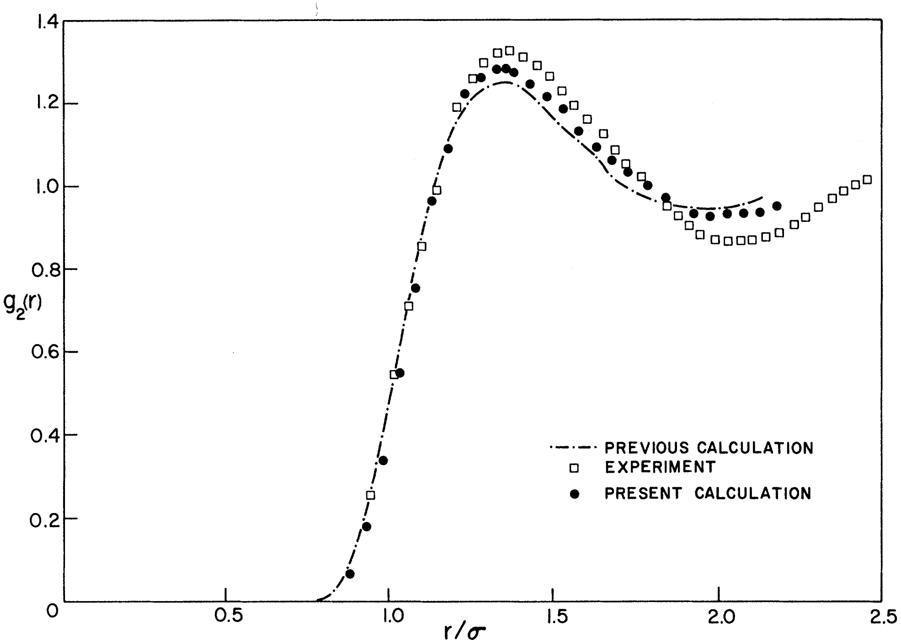

FIG. 1. Comparison of present and previous calculations of radial distribution function with experiment.

having larger values of m and n.

The use of this more flexible form of $w(r)$ led to better results than previous Monte Carlo calculations.[2–4] The improvement in the calculated $g_2(r)$ can been seen from Fig. 1, where the experimental $g_2(r)$ of Achter and Meyer[13] is compared with the present calculation and with the previous calculation.[4] Both theoretical curves represent calculations of $g_2(r)$ for the equilibrium density and for that value of the variational parameter which minimizes the expectation value of the energy using the LJ potential. The present calculation reproduces more of the structure of the experimental $g_2(r)$, particularly in the neighborhood of the first maximum. For most of the two-body potentials considered, the computed E_0 was lower and its density dependence in better agreement with experiment than the previous calculation,[4] as will be seen in detail for the various potentials.

a. LJ *potential.* The results of the present calculation of the density dependence of E_0/N using the LJ potential are contained in Fig. 2, where they may be compared both with experiment and with previous calculations.[2–4] The evaluation of the experimental energies is as discussed in Ref. 4, except that we have here used the better value for $E_0(\rho_0)/N$ of $-7.14\,^\circ\mathrm{K} = -0.699\,\epsilon_{\mathrm{LJ}}$. It is evident that although the minimum, including three-body terms, of the present calculation of the ground-state energy ($-0.568\,\epsilon_{\mathrm{LJ}}$) is about the same as before[4] ($-0.572\,\epsilon_{\mathrm{LJ}}$), the present calculated equilibrium density is about 3% higher than before and the density dependence of E_0/N is in better agreement with experiment.

b. Beck potential. Our results calculated with potential recently proposed by Beck[8] are contained in Fig. 3. The minimum (including the three-body terms) calculated energy, $-0.550\,\epsilon_{\mathrm{LJ}}$, is about the same as the minimum energy calculated using the LJ potential because the depth of Beck's potential is only about 1% greater than that of the LJ potential; the calculated equilibrium density is about 6% lower, and hence in worse agreement with experiment, than that calculated with the LJ potential, presumably because the minimum of the Beck potential occurs for a 2% larger value of

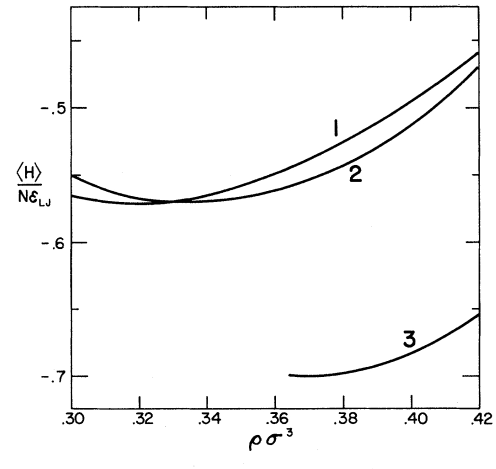

FIG. 2. Density dependence of ground-state energy. Curve 1: previous calculation, LJ potential. Curve 2: present calculation, LJ potential. Curve 3: experimental.

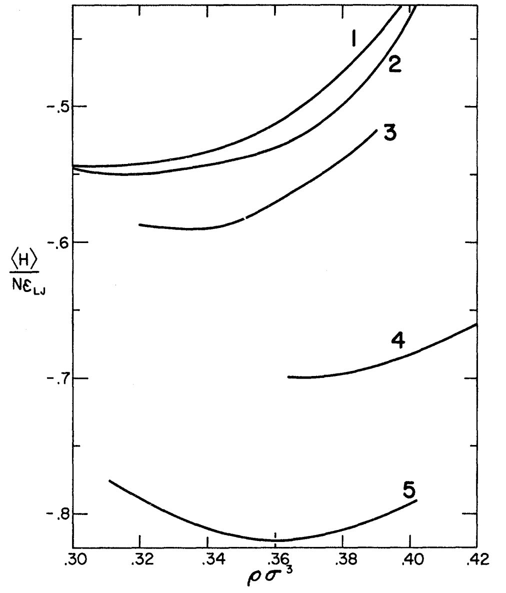

FIG. 3. Density dependence of ground-state energy. Curve 1: MDD-2 potential. Curve 2: Beck potential. Curve 3: highest values obtained with original Bruch-McGee potentials. Curve 4: experimental. Curve 5: lowest values obtained with original Bruch-McGee potentials.

the interparticle separation.

c. Bruch-McGee potentials. The original Bruch-McGee potentials[9] consist of an exponential fit to the the short-range repulsion, the correct long-range behavior, $-(C_6/r^6+C_8/r^8)$, and three different analytic forms near the minimum: the Frost-Musulin (FDD - 1), Morse (MDD - 1), and Rydberg (RYDD - 1) forms. These potentials are characterized by a depth ϵ occurring at separation r_m, as follows:

$$\epsilon = (1.73 \pm 0.11)\times 10^{-15}\text{ erg},\quad r_m = (2.981 \pm 0.022)\text{ Å} \quad \text{for FDD} - 1,$$

$$\epsilon = (1.675 \pm 0.11)\times 10^{-15}\text{ erg},\quad r_m = (2.975 \pm 0.022)\text{ Å} \quad \text{for MDD} - 1,$$

$$\epsilon = (1.80 \pm 0.10)\times 10^{-15}\text{ erg},\quad r_m = (2.97 \pm 0.020)\text{ Å} \quad \text{for RYDD} - 1, \quad .$$

In a later paper,[10] Bruch and McGee found better agreement with virial coefficient data by using the Morse form and the MDD - 2 parameters: $\epsilon = 1.484 \times 10^{-15}$ erg, $r_m = 3.0238$ Å.

We calculated E_0/N as a function of ρ for different values of the parameters ϵ and r_m for the three original Bruch-McGee potentials. The results for E_0/N using some of the deeper of these potentials lie below the experimental ground-state energy, as may be seen in Fig. 3, where the envelope of $E_0(\rho)/N$ is plotted. Curve 3 is obtained using the MDD - 1 potential with $\epsilon = 1.565\times 10^{-15}$ erg and $r_m = 2.997$ Å; Curve 5 is obtained with the RYDD - 1 potential with $\epsilon = 1.90\times 10^{-15}$ erg, $r_m = 2.95$ Å.

Since our calculation is a strict variational calculation, it follows that there should not be values of $E_0(\rho)/N$ below experiment. Accordingly, we were able to determine maximum values of the well depth, which we denote by $\epsilon_{\max}$, as a function of r_m as those that yielded the minimum calculated E_0 equal to the experimental ground-state energy, $-0.699\ \epsilon_{LJ}$. We found that at fixed r_m the calculated equilibrium density was essentially independent of ϵ, but that at fixed ϵ the calculated minimum ground-state energy varied considerably with r_m. Accordingly, the $\epsilon_{\max}$ for the three potentials varies considerably with r_m, as can be seen from Table II.

We also used the newer Bruch-McGee potential,[10] MDD - 2, and the results are shown in Fig. 3. As before,[4] it yielded ground-state energies a bit higher and equilibrium energies a bit lower than the LJ potential.

IV. SUMMARY AND CONCLUSIONS

We have found that the best variational ground-state wave function for liquid He^4 of the family $w(r) = (a/r)^m \pm (a/r)^n$ is for $m = 5$, $n = 4$, with the sign of both terms positive, and that this form leads to an improved agreement between the calculated and experimentally observed radial distribution functions. In addition, we have found a considerable variation of, first, the calculated energy and, second, its density dependence, with the form of the potential used. Both of these two features may be expected to be useful in determining the helium-helium interaction, and we have used the first of them (plus the fact that our calculation is a strict variational procedure) to set limits on the well depth of some of the proposed potentials.

The second feature, the sensitivity of the cal-

TABLE I. Maximum Depth of Bruch-McGee potentials as a function of location of minimum.

Potential	r_m(Å)	$\epsilon_{\max}(10^{-15}\text{ erg})$
FDD-1	2.958	1.66
	2.980	1.74
	3.002	1.82
MDD-1	2.953	1.655
	2.975	1.71
	2.997	1.77
RYDD-1	2.95	1.65
	2.97	1.71
	2.99	1.79

culated density dependence (and hence the calculated pressure) to the location of the minimum of the potential, is potentially even more useful in that the second virial coefficient depends more on the shape of the bowl than on its location. However, we feel that this feature of the calculations will be useful only when more definitive calculations have been done, because the possibility that all the variational calculations (including the present one) have a wrong density dependence (even if the correct potential were used) cannot be ruled out. It is certainly true, for example, that different calculations, e.g., that of Massey and Woo[1] and the present one, both using the LJ potential, produce rather different density dependence, and we do not feel that the density dependence of the calculations done to date is sufficient to warrant any statement as to which of the potentials is most accurate.

ACKNOWLEDGMENTS

The author is indebted to Dr. J. A. Barker, Dr. M. L. Klein, Dr. T. R. Koehler, and Dr. I. J. McGee for useful discussions. The hospitality of the Chemistry Division of the National Research Council Laboratories, Ottawa, while this manuscript was in preparation is greatly appreciated.

---

*Work supported in part by a grant from the National Research Council of Canada.

†Present address.

[1] W. E. Massey and C. W. Woo, Phys. Rev. 164, 256 (1967).

[2] W. L. McMillan, Phys. Rev. 138, A442 (1965).

[3] D. Schiff and L. Verlet, Phys. Rev. 160, 208 (1967).

[4] R. D. Murphy and R. O. Watts, J. Low Temp. Phys. 2, 507 (1970).

[5] J.-P. Hansen, Phys. Letters 34A, 25 (1971).

[6] J. A. Barker and A. Pompe, Australian J. Chem. 21, 1683 (1968).

[7] M. V. Bobetic and J. A. Barker, Phys. Rev. B2, 4169 (1970).

[8] D. E. Beck, Mol. Phys. 14, 311 (1968).

[9] L. W. Bruch and I. J. McGee, J. Chem. Phys. 46, 2959 (1967).

[10] L. W. Bruch and I. J. McGee, J. Chem. Phys. 52, 5884 (1970).

[11] P. J. Leonard (unpublished).

[12] R. D. Murphy and J. A. Barker, Phys. Rev. A 3, 1037 (1971).

[13] E. K. Achter and L. Meyer, Phys. Rev. 188, 291 (1968).

PHYSICAL REVIEW A VOLUME 5, NUMBER 1 JANUARY 1972

Growth of He^3 Layers from Surfaces of Nearly Saturated Solutions of He^3 in Superfluid He^4

W. F. Saam
Department of Physics, The Ohio State University, Columbus, Ohio 43210
(Received 7 September 1971)

The problem of the growth of the He^3 phase from a free surface of a nearly saturated solution of He^3 in superfluid He^4 at zero temperature is considered. Using a Fermi-liquid theory modified to account for the finite thickness of the He^3 phase by introducing a distortion of the Fermi surface, we find that the number of He^3 layers N_L in the He^3 phase increases as the He^3 chemical potential μ_3 approaches its bulk value μ_3^0 as $N_L \sim (\mu_3^0 - \mu_3)^{-1/2}$. This prediction is in agreement with recent experimental results of Guo, Edwards, Sarwinski, and Tough.

I. INTRODUCTION

Here we consider the problem of the growth, at zero temperatures, of He^3 layers from a free, plane surface of a nearly saturated solution of He^3 in superfluid He^4. In order to understand the nature of this problem, it is useful to look qualitatively at what happens as He^3 atoms are added to a bath of superfluid He^4 which has a free, plane surface, and which initially contains no He^3. Both experimental[1–3] and theoretical[4] evidence indicate the existence of bound states for the He^3 atoms on the He^4 surface. As shown by Guo, Edwards, Sarwinski, and Tough,[3] as the He^3 atoms are added at 0 °K they first fill up the surface states until approximately one layer of He^3 is deposited on the He^4 surface, Subsequently, added He^3 atoms spill over into the bulk He^4, increasing the bulk He^3 concentration from zero toward its limiting value of 6.6% at the phase-separation curve. Now, the point on the phase-separation curve at $T = 0$ °K is the point at which the He^3 chemical potential μ_3 is equal to its value μ_3^0 in pure bulk He^3. As μ_3 approaches μ_3^0, then, some of the He^3 atoms being added begin to build a second layer of He^3 on the surface, followed by a third, and so on. A phase of pure He^3 grows on the surface of the solution, the number of layers N_L in this phase approaching