

Binding of spin-polarized hydrogen to the free surface of liquid helium

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The binding energy of a single H, D, or T atom to the free surface of liquid ${}^4\text{He}$ has been calculated by a variational method. The calculation is of the Feynman-Lekner form, generalized to include the difference between the H-He and He-He interatomic potentials. The results depend on various properties of the pure ${}^4\text{He}$ surface: the density and kinetic energy distribution, and the two body correlation function. These have been obtained partly from data on atomic scattering at the surface, and partly from a theoretical model which emphasizes the asymptotic behavior far above the surface. It is believed that the assumptions about the ${}^4\text{He}$ surface lead to genuine lower limits for the H, D, and T binding energies. The binding of H to the surface is at least 0.6 K, which is large enough to be important for low-temperature experiments on spin-polarized hydrogen.

I. INTRODUCTION

The possibility of studying the low-temperature properties of the hydrogen isotopes condensed as atoms, rather than molecules, has attracted some interest in recent years.¹⁻¹² Combination into molecules will not occur if the hydrogen is completely spin polarized ($\text{H}\uparrow$) and if it is stabilized against spin flips. A recent estimate^{6,8} is that a magnetic field B , and temperature T , such that $B/T > 10^6$ G/K should achieve this, provided there are no impurities and the density is sufficiently low. The interaction potential between polarized $\text{H}\uparrow$ is very weak¹³ and it is predicted^{2,3,5} that even at 0 K it will form a gas rather than a liquid up to a solidification pressure of perhaps 50 atmospheres.^{4,5} Since $\text{H}\uparrow$ obeys Bose statistics it is clearly of great interest to study the Bose-Einstein condensation and superfluidity in $\text{H}\uparrow$ gas.^{3-5,7} In the analogous case of $\text{D}\uparrow$, which obeys Fermi statistics, it may form a gas^{2,3} at low pressure condensing into a Fermi liquid at higher pressures.⁵ Spin-polarized tritium, $\text{T}\uparrow$, is predicted to have a ground state which is liquid at zero pressure.³

The problem of finding a completely neutral, non-magnetic container for spin-polarized hydrogen has received some attention, and a vessel lined with a thick film of superfluid ${}^4\text{He}$ seems to be a good possibility.⁸ Recently Miller¹⁴ has calculated that a single H atom dissolved in liquid ${}^4\text{He}$ at zero pressure has a positive energy of ~ 40 K compared to the energy of H in vacuum. This constitutes an ample barrier to the penetration of $\text{H}\uparrow$ through the helium film, at least from $\text{H}\uparrow$ gas at low density and temperature. Using values for the volume, pressure, and energy of solid $\text{H}\uparrow$ from Refs. 4 and 5, the chemical potential at 0 K of $\text{H}\uparrow$ near solidification appears to be about 60 K. Even in this case, a vessel lined with a ${}^4\text{He}$ film might still be an adequate container since the ${}^4\text{He}$

film would then be denser than at zero pressure (and presumably crystalline). However, even with an adequate container, it may not be possible to produce solid or very dense $\text{H}\uparrow$ since recent calculations^{11,12} indicate that stability against spin flips at high density requires a very large magnetic field, even at 0 K. In early experiments then, the $\text{H}\uparrow$ concentration is likely to be very low. The fact that $\text{H}\uparrow$ can be *adsorbed* on the surface of the containing helium film is therefore of some practical interest and importance. If the concentration of $\text{H}\uparrow$ adsorbed on the surface becomes large enough, the formation of H_2 molecules might begin, with disastrous results!

The possibility of a bound state for hydrogen on the surface of ${}^4\text{He}$, analogous to the binding of ${}^3\text{He}$ on ${}^4\text{He}$, was pointed out by Stwalley,⁸ who estimated the binding energy to be about 1.5 K. No details of the calculation were given. A second unpublished calculation by Stwalley gave 0.6 K for the binding energy.¹⁵ Another unpublished estimate was made by Miller,¹⁶ using a variational method with a very simple trial function, one in which correlations between the H atom and the He atoms in the liquid were completely neglected. The calculation indicated that the binding of $\text{H}\uparrow$ to ${}^4\text{He}$ was less than 0.01 K and therefore of no practical consequence. In the present paper we also use a variational method, with a wave function which includes correlations, to calculate the binding energies for $\text{H}\uparrow$, $\text{D}\uparrow$, and $\text{T}\uparrow$. We obtain a value for the binding energy for $\text{H}\uparrow$ which is comparable to those found by Stwalley. Since it is variational, the theory should give reliable lower limits for the binding energies. However, the calculation requires knowledge of the ground-state properties of the ${}^4\text{He}$ surface: the density profile (one-particle density function), the two-particle density function, and the kinetic energy density, all in the surface region. At present none of these quantities is known very pre-

cisely, although we have tried to use, whenever possible, "conservative" assumptions about them so that the resulting estimates for the binding energies are genuine lower limits. We have also used information from ^4He scattering data to supplement theoretical calculations. If and when it becomes possible to study the adsorption of the hydrogen isotopes on ^4He , the measurement of the binding energy should give some useful information about the properties of the ground-state ^4He surface. It will also be interesting to study finite concentrations of adsorbed $\text{H}\uparrow$, $\text{D}\uparrow$, or $\text{T}\uparrow$, since these will form quasi-two-dimensional Bose and Fermi fluids.¹⁷

II. THEORY

To calculate the binding of a foreign particle of mass m at the surface of liquid helium we use an extension of the Feynman-Lekner^{18,19} variational method. This has been very successful in calculations of the binding of ^3He to the ^4He surface.²⁰⁻²³ The Feynman trial wave function for a single-impurity atom (at \bar{r}_1) and $N-1$ ^4He atoms (at $\bar{r}_2, \dots, \bar{r}_N$) is

$$\psi(\bar{r}_1, \dots, \bar{r}_N) = f(\bar{r}_1)\psi_0(\bar{r}_1, \dots, \bar{r}_N) \quad (1)$$

Here $f(\bar{r}_1)$ is to be varied so as to minimize the energy, and $\psi_0(\bar{r}_1, \dots, \bar{r}_N)$ is the wave function for N helium atoms in their ground state at zero pressure and with a free liquid surface. The wave function ψ defined by Eq. (1) has the same correlations between the impurity atom and the ^4He atoms as between ^4He in the ground state ψ_0 . The ^4He ground-state wave function ψ_0 is real and symmetric, and it is the lowest eigenstate of the Hamiltonian H_0

$$H_0\psi_0 = E_0\psi_0 \quad (2)$$

$$H_0 = -\frac{\hbar^2}{2m_4} \sum_{i=1}^N \nabla_i^2 + \frac{1}{2} \sum_{i \neq j}^N v_0(|\bar{r}_i - \bar{r}_j|) \quad (2)$$

Here $v_0(r)$ is the interatomic potential between two helium atoms. The ^4He ground-state energy E_0 is approximately $-NL_4$, where L_4 is the latent heat at absolute zero, but it also contains the surface energy. The experimental value of L_4 is $L_4/k_B = 7.16$ K. The Hamiltonian for the trial wave function (1), which has particle 1 replaced by a foreign atom of mass m , is

$$H = H_0 + \Delta H_1 \quad (3)$$

where

$$\Delta H_1 = -\frac{\hbar^2}{2m_4} \left(\frac{m_4}{m} - 1 \right) \nabla_1^2 + \sum_{j>1}^N v_d(|\bar{r}_j - \bar{r}_1|) \quad (4)$$

and the "difference potential" $v_d(r)$ is the He-

impurity potential minus the He-He potential

$$v_d(r) = v(r) - v_0(r) \quad (5)$$

To find an approximation to the ground state of the impurity atom-liquid ^4He system the expectation value of the energy

$$\langle E \rangle = \int \psi^* H \psi d\bar{r}_1 \cdots d\bar{r}_N / \int \psi^* \psi d\bar{r}_1 \cdots d\bar{r}_N \quad (6)$$

is minimized with respect to variations in $f(\bar{r}_1)$. The resulting Euler-Lagrange equation can be written in the form of a single-particle Schrödinger equation if the following substitution is made:

$$f(\bar{r}_1) = \phi(\bar{r}_1)/a(\bar{r}_1) \quad (7)$$

where the "amplitude" $a(\bar{r}_1)$ is related to the particle density in the original ^4He ground state

$$a^2(\bar{r}_1) = \rho(\bar{r}_1)/\rho_0 \quad (8)$$

$$\rho(\bar{r}_1) = N \int \psi_0^2 d\bar{r}_2 \cdots d\bar{r}_N / \int \psi_0^2 d\bar{r}_1 \cdots d\bar{r}_N$$

The bulk density ρ_0 is the value of $\rho(\bar{r}_1)$ with \bar{r}_1 deep inside the liquid. With the substitution (7) the Euler-Lagrange equation becomes

$$-\frac{\hbar^2}{2m} \nabla_1^2 \phi(\bar{r}_1) + V_{\text{eff}}(\bar{r}_1) \phi(\bar{r}_1) = (E - E_0 - L_4) \phi(\bar{r}_1) \\ = \epsilon \phi(\bar{r}_1) \quad (9)$$

The "effective potential" $V_{\text{eff}}(\bar{r}_1)$ is related to properties of the ^4He ground state ψ_0 . For convenience, it includes a term $-L_4$ so that the impurity energy ϵ is referred to the state in which the impurity is in the vacuum above the liquid. The probability density for the impurity particle in the state ψ is given by

$$\int |\psi|^2 d\bar{r}_2 \cdots d\bar{r}_N / \int |\psi|^2 d\bar{r}_1 \cdots d\bar{r}_N \\ = |\phi(\bar{r}_1)|^2 / \int |\phi(\bar{r}_1)|^2 d\bar{r}_1 \quad (10)$$

so that $\phi(\bar{r}_1)$ is truly analogous to a single-particle wave function with the impurity atom in a potential V_{eff} .

The expression for V_{eff} contains terms related to the one-particle, two-particle, and kinetic energy densities in the ^4He ground state

$$V_{\text{eff}}(\bar{r}_1) = -L_4 + \frac{(\hbar^2/2m)[\nabla_1^2 a(\bar{r}_1)]}{a(\bar{r}_1)} + \left(\frac{m_4}{m} - 1 \right) t(\bar{r}_1) \\ + \int \rho(\bar{r}_2) g(\bar{r}_1, \bar{r}_2) v_d(|\bar{r}_1 - \bar{r}_2|) d\bar{r}_2 \quad (11)$$

Here $g(\bar{r}_1, \bar{r}_2)$ is the ^4He two-particle correlation func-

tion defined by

$$\rho(\vec{r}_1)\rho(\vec{r}_2)g(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1, \vec{r}_2) , \quad (12)$$

where the two-particle density function is

$$\rho(\vec{r}_1, \vec{r}_2) = \frac{N(N-1) \int \psi_0^2 d\vec{r}_3 \cdots d\vec{r}_N}{\int \psi_0^2 d\vec{r}_1 \cdots d\vec{r}_N} . \quad (13)$$

The function $t(\vec{r}_1)$ is the local kinetic energy density divided by the local density, i.e., the kinetic energy per particle in the ^4He ground state

$$t(\vec{r}_1) = \frac{(\hbar^2/2m_d) \int \psi_0 \nabla_1^2 \psi_0 d\vec{r}_2 \cdots d\vec{r}_N}{\int \psi_0^2 d\vec{r}_2 \cdots d\vec{r}_N} . \quad (14)$$

For the special case of a helium impurity $v_d=0$ and Eq. (11) reduces to the effective potential used by Saam,²⁰ Shih and Woo,²¹ and Chang and Cohen²² to calculate the binding of ^3He to the surface.

We shall assume the free surface of the liquid to be planar and situated near $z=0$ with the liquid occupying the region $z < 0$. From symmetry it is clear that a , t , and V_{eff} depend only on z_1 , the z coordinate of \vec{r}_1 , and that

$$\rho(\vec{r}_1, \vec{r}_2) = \rho(z_1, z_2, |\vec{r}_1 - \vec{r}_2|) . \quad (15)$$

With the appropriate choice of x axis, the impurity effective wave function ϕ can be written

$$\phi(\vec{r}_1) = e^{ik_x x} \phi(z_1) \text{ so that}$$

$$\epsilon = \epsilon_z + \hbar^2 k_x^2 / 2m , \quad (16)$$

where ϵ_z is the energy from the solution of

$$-\frac{\hbar^2}{2m} \frac{d^2 \phi(z_1)}{dz_1^2} + V_{\text{eff}}(z_1) \phi(z_1) = \epsilon_z \phi(z_1) . \quad (17)$$

If the lowest eigenstate of this one-dimensional equation is lower than the continuum of states in the vacuum ($z \rightarrow \infty$) and in the interior of the liquid ($z \rightarrow -\infty$), then we have one or more surface bound states. The problem of calculating V_{eff} so that the binding energy (if any) can be determined is discussed in Sec. III. We note that the theory outlined here does not include "backflow" effects and that, from Eq. (16), the effective mass of the impurity quasiparticle is the same as its real mass. For adsorbed ^3He the experimental effective mass²³ is $1.45 m_3$ (compared to about $2.3 m_3$ in bulk ^4He). However, for adsorbed H the effect of back flow should be very weak since, as we shall see, the wave function of the bound state has its maximum much further above the liquid where the ^4He density is very low.

III. CALCULATIONS OF THE EFFECTIVE POTENTIAL

The interatomic potential between a hydrogen and a helium atom $v(r)$ has been determined by Toen-

TABLE I. Lennard-Jones parameters for the helium-helium, helium-hydrogen, and the "difference" potential (see text).

	ϵ (K)	σ (Å)
He-He	10.22	2.556
He-H	6.57	3.19
Difference	2.56	3.42

nies, Welz, and Wolf²⁴ from the scattering of an H or D atomic beam by He together with theoretical calculations. In what follows we assume for simplicity that both $v(r)$ and the He-He potential²⁵ $v_0(r)$ are of the Lennard-Jones form

$$\begin{aligned} v_0(r) &= 4\epsilon_0(\sigma_0^{12}/r^{12} - \sigma_0^6/r^6) , \\ v(r) &= 4\epsilon(\sigma^{12}/r^{12} - \sigma^6/r^6) . \end{aligned} \quad (18)$$

One advantage of this assumption, apart from its simplicity, is that we get a good approximation to the Van der Waals potential, which varies as $1/r^6$, at large distances. This is important if the impurity particle binds at a large distance above the liquid surface, as we expect for hydrogen. If v and v_0 are Lennard-Jones, then the "difference potential" $v_d(r)$ defined in Eq. (5), is also of the Lennard-Jones form (although, in principle, neither σ_d^6 nor ϵ_d need be positive)

$$\begin{aligned} v_d(r) &= 4\epsilon_d(\sigma_d^{12}/r^{12} - \sigma_d^6/r^6) , \\ \sigma_d^6 &= (\epsilon\sigma^{12} - \epsilon_0\sigma_0^{12})/(\epsilon\sigma^6 - \epsilon_0\sigma_0^6) , \\ \epsilon_d &= (\epsilon\sigma^6 - \epsilon_0\sigma_0^6)/\sigma_d^6 . \end{aligned} \quad (19)$$

The data for $v(r)$ have been fitted to the Lennard-Jones form by Miller.¹⁴ The parameters for v , v_0 , v_d are given in Table I. For hydrogen-helium the differ-

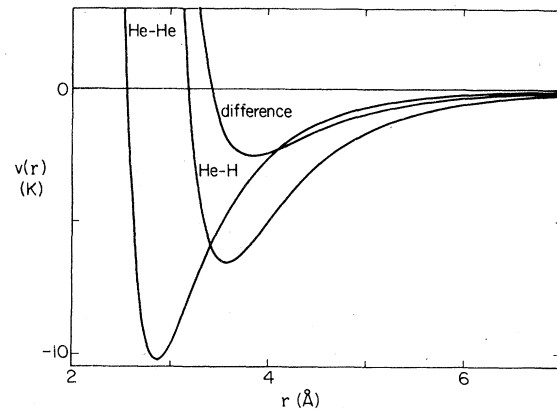


FIG. 1. Lennard-Jones potentials between two helium atoms (labeled He-He), and between a helium and a hydrogen atom (He-H). The "difference" potential is the He-He potential subtracted from the He-H potential.

ence potential is of the conventional type with ϵ_d and σ_d^6 positive. Figure 1 shows the He-He, He-H, and the difference potential.

A. Effective potential for ^4He

In calculating the various terms in the effective potential V_{eff} [see Eq. (11)] it is important in the surface hydrogen problem to get the asymptotic behavior in the vacuum ($z \rightarrow \infty$) as nearly correct as possible. As we have mentioned before, this is because the hydrogen isotopes are expected to bind rather far above the surface where the ^4He density $\rho(z)$ is very small.

If we consider the terms in V_{eff} in turn, only the first two are nonzero if we apply the theory to a ^4He atom ($m = m_4, v_d = 0$) treated as an "impurity". In this case

$$V_{\text{eff}}(z_1) = (\hbar^2/2m_4)a''(z_1)/a(z_1) - L_4 \equiv V_4(z_1) . \quad (20)$$

In the interior of the liquid ($z \rightarrow -\infty$), where the density is uniform, $a'' = 0$ and $V_{\text{eff}} \rightarrow -L_4$. The asymptotic behavior of $V_4(z)$ above the liquid, as $z \rightarrow \infty$, has been discussed by Edwards and Fatouros²⁶ (EF) who have used the form

$$\begin{aligned} a(z) &= 1/(e^{\beta z} + 1) , \\ p(z) &= \beta z + \gamma + (\lambda/4\beta)/(z^2 + \delta^2) . \end{aligned} \quad (21)$$

In this equation the various parameters are defined as follows: The inverse length $\beta = 1.087 \text{ \AA}^{-1}$ is defined so that

$$\hbar^2\beta^2/2m_4 = L_4 . \quad (22)$$

The length $\lambda \approx 20 \text{ \AA}$ is such that the $1/z^3$ Van der Waals attraction between the liquid and a He atom above the liquid is given by

$$\frac{-\alpha_0}{z^3} = \frac{-\frac{2}{3}\pi\rho_0\epsilon_0\sigma_0^6}{z^3} = \frac{-\hbar^2\lambda}{2m_4z^3} . \quad (23)$$

The standard values²⁷ for ϵ_0 and σ_0 (Table I) give $\lambda = 21.5 \text{ \AA}$. In common with Ref. 26 we have used $\lambda = 20 \text{ \AA}$ as a rough compromise between this and the theoretical²⁸ Van der Waals potential at large distances which gives $\lambda = 19.2 \text{ \AA}$. The other parameters $\gamma = -2.5$, $\delta^2 = 8.5 \text{ \AA}^2$, were adjusted by EF to give a good fit to the elastic scattering probability for ^4He atoms striking the liquid surface.

The amplitude $a(z)$ in Eq. (21) is constructed to give the correct asymptotic behavior deep in and far above the liquid

$$\begin{aligned} a(z \rightarrow -\infty) &= 1 , \quad V_4(z \rightarrow -\infty) = -L_4 , \\ a(z \rightarrow \infty) &= e^{-\beta z} , \quad V_4(z \rightarrow \infty) = -\alpha_0/z^3 . \end{aligned} \quad (24)$$

Since it gives a good fit to the elastic scattering of ^4He , which takes place mainly above the liquid surface, we believe that the term in a''/a in V_{eff} is very

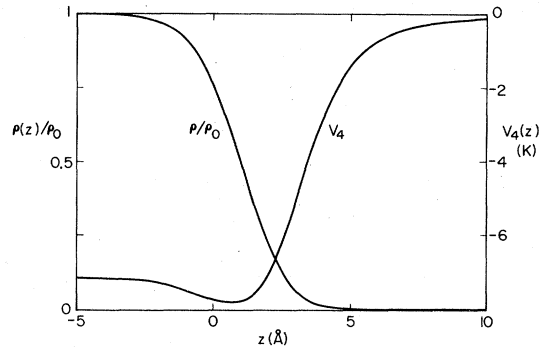


FIG. 2. Density profile $\rho(z)/\rho_0$ for the ^4He surface, and the corresponding effective potential for a ^4He atom $V_4(z)$ according to the model of Edwards and Fatouros (Ref. 26). The effective potential fits the elastic scattering of ^4He from the surface.

well determined as far as the hydrogen problem is concerned. A discussion of the use of the unsymmetrized wave function (1) to describe ^4He scattering is given in EF. However we remark here that although $V_4(z)$, shown in Fig. 2, has a shallow minimum near the surface there is no surface bound state. Moreover the "single-particle" Schrödinger equation (9) gives the exact result for the ground state of a ^4He "impurity". This is $\epsilon = -L_4$, $\phi(\vec{r}_1) = a(\vec{r}_1)$ which corresponds to $f(\vec{r}_1) = 1$, $\psi = \psi_0$.

B. Effective potential for ^3He

We next consider the term in V_{eff} proportional to the kinetic energy $t(z_1)$ in the liquid- ^4He ground state. This term is important in the binding of ^3He to the surface; from Eq. (11) the effective potential for ^3He is

$$\begin{aligned} V_{\text{eff}}(z_1) &= \frac{(\hbar^2/2m_3)a''(z_1)}{a(z_1)} - L_4 + \left(\frac{m_4}{m_3} - 1\right)t(z_1) \\ &= \left(\frac{m_4}{m_3}\right)V_4(z_1) + \left(\frac{m_4}{m_3} - 1\right)[t(z_1) + L_4] \\ &\equiv V_3(z_1) . \end{aligned} \quad (25)$$

The asymptotic behavior of $t(z_1)$ can be determined as follows. Far above the liquid surface (z_1 large), $V_3(z_1)$ must be the same as the real Van der Waals attraction for a helium atom above the liquid

$$V_3(z_1) = V_4(z_1) \approx -\alpha_0/z_1^3 , \quad (z_1 \text{ large}) . \quad (26)$$

Substitution from Eq. (26) into Eq. (25) yields

$$\begin{aligned} t(z_1) &= -V_4(z_1) - L_4 \\ &= -(\hbar^2/2m_4)a''(z_1)/a(z_1) , \quad (z_1 \text{ large}) . \end{aligned} \quad (27)$$

Deep inside the liquid, $V_4(z_1 \rightarrow -\infty) = -L_4$ and

$$V_3(z_1 \rightarrow -\infty) = -E_3. \quad (28)$$

Here $-E_3$ is the energy of the lowest ^3He quasiparticle state in bulk ^4He (at zero pressure). Experimentally $E_3/k_B = 2.785$ K.²⁹ Substituting in Eq. (25) gives

$$t(z_1 \rightarrow -\infty) \equiv t_0 = (L_4 - E_3)/(m_4/m_3 - 1). \quad (29)$$

Substituting $L_4/k_B = 7.16$ K, we find $t_0/k_B = 13.34$ K. Since Eq. (29) represents a variational calculation of E_3 in terms of t_0 , the results should properly be expressed as $t_0/k_B \geq 13.34$ K. This agrees very well recent accurate theoretical calculations³⁰ of t_0 (which give $t_0/k_B = 13.6 \pm 0.12$ K). In what follows however we shall use the equality $t_0 = 13.34$ K in order that Eq. (28) be consistent with the experimental value of E_3 .

To obtain a formula for the dependence of $t(z_1)$ on z_1 as we approach the surface from below, we follow Saam²⁰ and note that the change in the kinetic energy per particle will be due mainly to the change in the local density. Thus $t(z_1)$ can be found from the pressure variation of $L_4 - E_3$ in the bulk liquid, which is related to the volume occupied by a ^3He atom in solution in bulk ^4He

$$\begin{aligned} \left(\frac{\rho_0}{t_0} \right) \frac{dt_0}{d\rho_0} &= \frac{(\rho_0/t_0)[d(L_4 - E_3)/d\rho_0]}{(m_4/m_3 - 1)} \\ &= \frac{(\rho_0/t_0)m_4s^2[d(L_4 - E_3)/d\rho]}{(m_4/m_3 - 1)} \\ &= \frac{(m_4s^2/t_0)\alpha_3}{(m_4/m_3 - 1)} \equiv n. \end{aligned} \quad (30)$$

In this equation we have used the fact that $dp/d\rho_0 = m_4s^2$, where s is the velocity of sound in ^4He at 0 K, and we have written the volume occupied by a ^3He atom in solution as $(1 + \alpha_3)/\rho_0$. Experimentally $\alpha_3 = 0.284$,²⁹ and $m_4s^2/k_B = 27.0$ K, so that the coefficient n is 1.76. In the region just below the surface of the liquid we shall assume that $t(z_1) \propto [\rho(z_1)]^n$ which leads to the equation

$$t(z_1) = t_0 a^{2n}(z_1), \quad (-z_1 \text{ large}). \quad (31)$$

To obtain an interpolation formula between Eqs. (27) and (31) which is valid for both positive and negative z_1 is rather simple. Both expressions for $t(z_1)$ become very small outside their approximate range of validity, so it is only necessary to add them together

$$t(z_1) = t_0 a^{2n}(z_1) - V_4(z_1) - L_4, \quad (\text{all } z_1). \quad (32)$$

Values for $t(z_1)$ from the expression are shown in Fig. 3, which also gives the two asymptotic contributions separately.

With the kinetic energy $t(z_1)$ determined by Eq. (32) we can substitute in Eq. (25) to obtain the ^3He

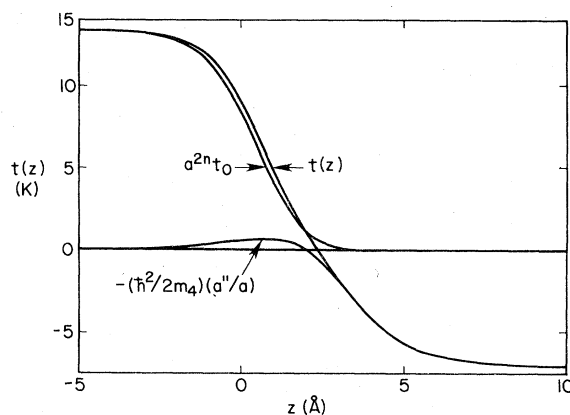


FIG. 3. Kinetic energy per atom $t(z)$ in the surface of ^4He as a function of height z . As explained in the text, the curve for $t(z)$ is interpolated as the sum of two contributions, one appropriate to variations in the density of the bulk liquid $a^{2n}t_0$, and one appropriate to the region above the liquid where the density is very small, $-(\hbar^2/2m_4)(a''/a)$. The origin for z is the same as in Fig. 2.

effective potential in the following simple form:

$$V_3(z_1) = V_4(z_1) + (m_4/m_3 - 1)t_0 a^{2n}(z_1). \quad (33)$$

This is shown in Fig. 4(b). The one-dimensional Schrödinger equation (17) with $V_3(z_1)$ from Eq. (33) has been solved numerically to find the ^3He bound states. We find only one bound state for which the binding energy (referred to vacuum) is 4.64 K. The wave function for the ^3He bound state is illustrated in Fig. 4(a). The experimental value²³ of the surface binding for ^3He is $E_3/k_B + (2.22 \pm 0.03)$ K $= (5.00 \pm 0.03)$ K so that our calculation can be regarded as quite satisfactory.

It is interesting to compare our results for ^3He with other calculations based on the Feynman-Lekner theory. Although this is a variational method, the calculated values of the energy are not necessarily above the true, experimental energy. This is caused by the uncertainty in the functions $V_4(z_1)$ and $t(z_1)$. Only if we had precise knowledge of $V_4(z_1)$ and $t(z_1)$ would we be sure that the calculated energy is an upper bound to the true energy. The earliest calculation of the ^3He bound-state energy was that of Saam,²⁰ who interpolated between the asymptotic behavior of $a(z_1)$ and $t(z_1)$ to obtain $V_3(z_1)$, just as we have done. However he did not include the $-\alpha_0/z^3$ Van der Waals attraction in the asymptotic behavior of either $a(z_1)$ or $t(z_1)$ at large z_1 . This may partly explain why his result for the binding energy, which is 4.05 K compared to vacuum, is not as close to experiment as ours. In addition we have the advantage of using the semiempirical Edwards-Fatouros expression for $V_4(z_1)$ which has been fitted to ^4He surface scattering data.

Completely microscopic calculations of $a(z_1)$ and

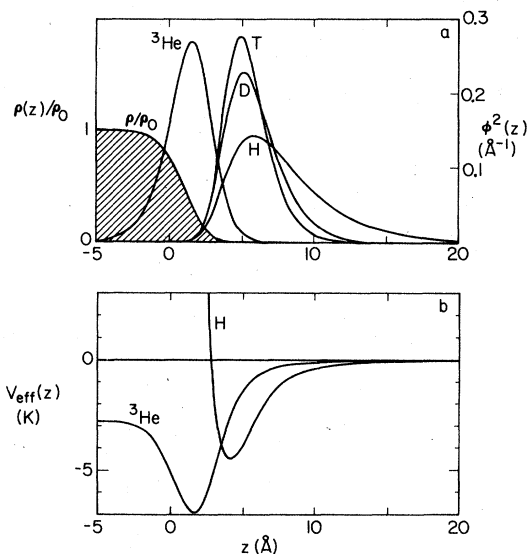


FIG. 4. Binding of the hydrogen isotopes to the surface of ${}^4\text{He}$. The lower graph shows the effective potential $V_{\text{eff}}(z)$ for hydrogen in the vicinity of the surface, with the effective potential for ${}^3\text{He}$ shown for comparison. The effective potentials for deuterium D and tritium T are the same as for H in the region which can be shown in the figure, although they are different in the region where $\rho/\rho_0 \sim 1$. The upper graph shows the density profile $\rho(z)/\rho_0$ for the ${}^4\text{He}$ surface (shaded, left-hand axis), and the normalized probability densities $\phi^2(z)$ for the surface bound states. The hydrogen isotopes are bound above the surface where the ${}^4\text{He}$ density is very low.

$t(z_1)$ have been made by Shih and Woo,²¹ who obtained 4.4 K for the binding energy, and Chang and Cohen,²² who found 5.1 K, which is very near, but slightly above the experimental value. Comparison with the calculation of Chang and Cohen is complicated by the fact that their theoretical value of the binding energy of the ${}^4\text{He}$ ground state L_4 is 7.43 K, larger than the experimental value 7.16 K. This is because they increased the He-He Lennard-Jones parameter ϵ_0 to $1.09\epsilon_0$ so that the theoretical equilibrium density of the liquid would be close to the experimental value.³¹ If we express the results in terms of $\epsilon_s = \epsilon + L_4$, the difference in binding energy between ${}^3\text{He}$ in the lowest surface state and ${}^4\text{He}$ in the ground state, then their result is $\epsilon_s = 2.347$ K, compared to our value of $7.16 - 4.64 = 2.52$ K and experiment $\epsilon = 2.15$ K.

A detailed comparison³² between our ${}^3\text{He}$ effective potential, expressed as $V_3(z) + L_4$, and that of Chang and Cohen is shown in Fig. 5. It is very satisfactory that the two potentials agree very well in the region of the minimum, where we have relied on our interpolation formula (32) for $t(z_1)$. Near the minimum our curve is very slightly wider and not quite so deep, but this is more than compensated by the differences

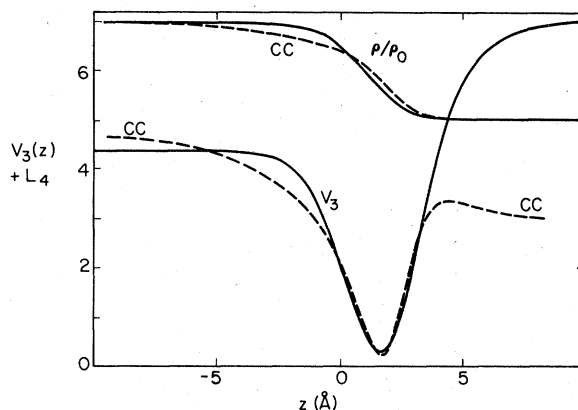


FIG. 5. Comparison between the density profiles (ρ/ρ_0 , with arbitrary vertical scale) and the ${}^3\text{He}$ effective potential $V_3(z)$ in the present work and those calculated by Chang and Cohen (shown dashed and labeled CC). The effective potential has been plotted with respect to the ${}^4\text{He}$ ground-state energy, i.e., as $V_3(z) + L_4$, since this is the quantity directly predicted by theory. The Chang and Cohen value of L_4 is substantially higher than ours, which has been fitted to experiment. The origin of the z axis for the Chang and Cohen curves has been shifted upward by 1.33 \AA , to make comparison easier. The Chang and Cohen effective potential is not correct at large z since it does not asymptotically approach their value of $L_4 = 7.43 \text{ K}$ as $z \rightarrow \infty$.

just below and just above the surface. Below the surface the Chang and Cohen $t(z_1)$ follows the relation expressed in Eq. (33) quite well, although their density profile is different from ours. Our profile is probably not very accurate in this region. Above the surface the large difference in $V_3(z)$ is due to the fact that the Chang and Cohen calculation is not asymptotically correct as z_1 becomes large. They estimated that if this were corrected it would cause a 0.15 K decrease in the binding, corresponding to $\epsilon_s = 2.50 \text{ K}$ which is close to our value.

C. Effective potential for the hydrogen isotopes

With the preceding results for $V_4(z)$ and $t(z_1)$, the effective potential for an impurity, such as a hydrogen atom, of mass m with a nonzero difference potential v_d becomes

$$V_{\text{eff}}(z_1) = V_4(z_1) + (m_4/m - 1)t_0 a^{2n}(z_1) + \int \rho(z_2) g(z_1, z_2, |\bar{\tau}_1 - \bar{\tau}_2|) \times v_d(|\bar{\tau}_1 - \bar{\tau}_2|) d\bar{\tau}_2. \quad (34)$$

The main problem in evaluating this expression stems from uncertainties in the correlation function. We shall use the approximation employed by Shih and Woo,²¹ Chang and Cohen,³¹ and others by substi-

tuting for the two-particle correlation function in the surface region the correlation function in the homogeneous liquid at a density $\bar{\rho}$ intermediate between the densities at z_1 and z_2

$$g(z_1, z_2, |\bar{r}_1 - \bar{r}_2|) \approx g(\bar{\rho}, |\bar{r}_1 - \bar{r}_2|) \quad (35)$$

Here

$$\bar{\rho} = [\rho(z_1) + \rho(z_2)]/2 \quad (36)$$

and $g(\rho, r)$ is the correlation function in homogeneous ^4He of density ρ . Substituting Eq. (35) into Eq. (34) the effective potential becomes

$$V_{\text{eff}}(z_1) = V_4(z_1) + (m_4/m - 1)t_0 a^{2n}(z_1) + \int_{-\infty}^{\infty} a^2(z_2) I(\bar{\rho}, |z_1 - z_2|) dz_2, \quad (37)$$

where

$$I(\bar{\rho}, |z_1 - z_2|) = \rho_0 \int_{|z_1 - z_2|}^{\infty} v_d(r) g(\bar{\rho}, r) 2\pi r dr \quad (38)$$

To evaluate I numerically we have employed the correlation functions $g(\bar{\rho}, r)$ between $\bar{\rho} = 0$ and $\bar{\rho} = \rho_0$, in steps of $0.1\rho_0$, calculated by Chang and Cohen,^{31,32} and used for their calculation of the density profile and $t(z)$. For the density profile $a^2(z_2) \equiv \rho(z_2)/\rho_0$ which appears in the integral in Eq. (36) we have used Eq. (21) in order to be consistent with the calculation of a''/a , which appears in $V_4(z_1)$. As discussed in EF,²⁶ although the density profile (21) has been adjusted to fit elastic scattering data it is probably not very accurate in the region where a^2 is not small compared to one. This is because the scattering of ^4He atoms from the surface is not sensitive to a''/a in this region. However, it is much more important in the present context that the formula be asymptotically correct for large z_1 where we expect the hydrogen surface state to be. With our choice of $a(z)$, it is easy to see that the effective potential at large z is equal, as it should be, to the Van der Waals attractive potential between the impurity and the liquid

$$V_{\text{eff}}(z_1 \rightarrow \infty) = -\alpha/z_1^3 = -(2\pi/3)\epsilon\rho_0\sigma^6/z_1^3 \quad (39)$$

We examine this point in more detail in Fig. 6 which compares the hydrogen V_{eff} with two calculations of the Lennard-Jones potential energy between a hydrogen atom and the helium liquid. For the first calculation we have assumed a density profile $\rho'(z)$ which falls linearly with z between $z_0 - b$ and $z_0 + b$

$$\rho'(z) = \begin{cases} \rho_0, & z \leq z_0 - b, \\ \frac{1}{2}\rho_0 \left(1 - \frac{z - z_0}{b}\right), & z_0 - b < z < z_0 + b, \\ 0, & z \geq z_0 + b. \end{cases} \quad (40)$$

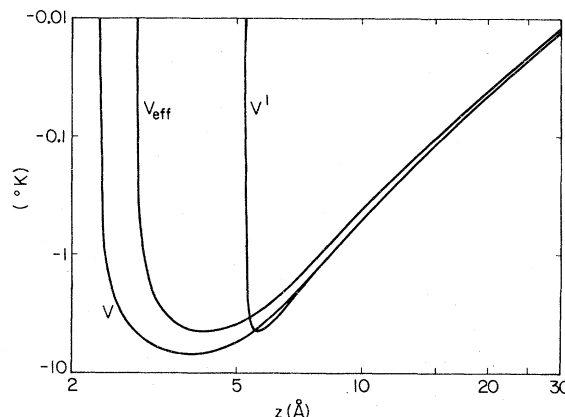


FIG. 6. Effective potential for H, $V_{\text{eff}}(z)$, compared with two calculations of the potential energy outside the liquid, $V'(z)$ and $V(z)$ from Eqs. (41) and (42).

The width of the profile $2b$ was set at 4.4 \AA , determined by fitting to the EF profile (21) at $\rho/\rho_0 = 0.9$ and $\rho/\rho_0 = 0.1$. The position of the dividing surface was made the same as for the EF profile at $z_0 = 1.0 \text{ \AA}$. The He-H interatomic potential $v(r)$ was then integrated over the liquid

$$V'(z_1) = \int \rho'(z_2) v(|\bar{r}_1 - \bar{r}_2|) d\bar{r}_2 = \int_{-\infty}^{z_0+b} \rho'(z_2) dz_2 \int_{|z_1 - z_2|}^{\infty} v(r) 2\pi r dr \quad (41)$$

The second version of the potential was calculated from the EF profile directly, using the correlation function

$$V(z_1) = \int \rho(z_2) g(\bar{\rho}, |\bar{r}_1 - \bar{r}_2|) v(|\bar{r}_1 - \bar{r}_2|) d\bar{r}_2 = \rho_0 \int_{-\infty}^{\infty} a^2(z_2) dz_2 \int_{|z_1 - z_2|}^{\infty} g(\bar{\rho}, r) v(r) 2\pi r dr \quad (42)$$

This expression is actually the expectation value of the potential energy of the hydrogen atom at \bar{r}_1 in our trial wave function (1). The two forms for the potential, Eqs. (41) and (42), are nearly the same for $z_1 \geq 8 \text{ \AA}$. As shown in Fig. 6 the effective potential $V_{\text{eff}}(z_1)$ approaches Eqs. (41) and (42) quite closely for large z , although the agreement is not quite perfect. This is partly because of the value $\lambda = 20 \text{ \AA}$ used in the a''/a term in the effective potential which, as remarked earlier, is not quite consistent with the value from the Lennard-Jones parameters. The discrepancy should have no effect on the accuracy of the hydrogen binding energy.

Figure 6 illustrates another point of greater interest and importance: The $V(z)$ and $V_{\text{eff}}(z)$ would approach each other much more rapidly if the origin of z for $V_{\text{eff}}(z)$ were moved approximately 1 \AA higher. This effect can probably be traced to the problem dis-

cussed in EF, that their profile is not "self-consistent." This means that, although their $a(z)$ gives an effective potential $V_4(z)$ which fits the elastic scattering data very well, $V_4(z)$ does not approach sufficiently closely to $V(z)$, as calculated from the He-He interatomic potential $v_0(z)$ with Eq. (42). If their profile could be modified to be self-consistent in this sense, while still retaining the fit to the scattering data, it might then be a good approximation to the real profile. For the purpose at hand, the calculation of the binding of hydrogen to the surface, the effect of such a modification would be to enhance the binding energy. This is easily seen from Eq. (34). The term $V_4(z)$ in V_{eff} would be displaced upward in z , producing a more attractive well. Modification of the profile would also affect the potential for ^3He and, from Eq. (33), the binding would probably be enhanced in this case too. In the present work since we are making a variational calculation of a lower bound on the hydrogen binding, it is not necessary to try to make the EF profile more nearly self-consistent.

IV. DISCUSSION

The bound state wave functions for H, D, and T that result from $V_{\text{eff}}(z_1)$ are illustrated in Fig. 4. The binding energies, which are lower bounds to the true energies, are given in Table II. There are second, weakly bound states for both T and D. As expected, the bound states are situated well above the liquid-helium surface. In this region the contribution to V_{eff} from the term in t_0 in Eq. (34) is small, so that the differences between V_{eff} for H, D, and T are insignificant. The binding energies should be regarded strictly as lower bounds since we believe that the actual binding energies for the hydrogen isotopes will be substantially larger. We have already discussed one reason for this: the fact that the EF profile is not "self-consistent." Other reasons which may be more important are as follows.

First, the correlation functions $g(\rho, r)$ that we have used are those calculated by Chang and Cohen³¹ using a modified Lennard-Jones parameter $1.09\epsilon_0$ for the He-He interatomic potential. This has the effect of making the contribution from the repulsive part of the difference potential substantially too large. One way to demonstrate this is to calculate $V_{\text{eff}}^{\text{bulk}}$, that is

TABLE II. Lower bounds for the binding of ^3He , H, D, and T to the surface of liquid ^4He (in kelvin).

	^3He	T	D	H
Lowest state	4.64	1.83	1.39	0.63
Second bound state	none	~ 0.015	10^{-4} – 10^{-3}	...

$V_{\text{eff}}(z_1)$ deep inside the liquid, where one needs only the bulk correlation function $g(\rho_0, r)$. Table III gives values for $V_{\text{eff}}^{\text{bulk}}$ calculated with the Chang and Cohen $g(r)$, and also those of Miller,¹⁴ and Massey and Woo.³³ Of these the Massey-Woo correlation function agrees best with experiment.

An additional error in our calculation is caused by the use of the approximation embodied in Eq. (35) rather than the true correlation function $g(z_1, z_2, r)$. Liu *et al.*³⁴ have criticized this approximation, since it gives different results for the density profile than their Monte Carlo calculations. The error introduced in the present calculation is very hard to assess. It may be helpful that the region of interest for the H isotopes is one of low- ^4He density. However if V_{eff} is calculated using $g(0, r)$ rather than $g(\bar{\rho}, r)$, the binding energies are increased substantially so that the approximation is necessary.

Of course the most fundamental reason why the calculated binding energies are only lower limits is because we are using a variational wave function. In particular the trial function that we have employed forces the hydrogen impurity to have the same correlations as a He atom. The true correlation function $g(\bar{T}_1, \bar{T}_2)$ for the hydrogen atom should have a larger nearest-neighbor distance than for the helium atoms, because the H-He interatomic potential has a repulsive core which is larger by about 0.8 Å. The lower mass and larger zero-point energy of H should also have some effect. Miller has calculated the He-H correlation function for a hydrogen atom dissolved in bulk ^4He . His calculation of V_{eff} for the interior of the liquid, given in Table III, is much lower than calculations using the He-He $g(r)$. There is little doubt that if the true He-H correlation function in the surface region could be taken into account it would greatly increase the binding of surface-adsorbed H. A variational calculation along these lines has recently been carried out by Guyer and Miller.³⁵ However their value for the binding energy of H (0.1 K) is much smaller than ours. This is because they were forced to make some restrictive approximations in solving their Euler-Lagrange equation. In particular, they assumed that the H-He correlation function in

TABLE III. V_{eff}/k_B for a hydrogen atom in bulk ^4He , calculated with different correlation functions $g(r)$.

Correlation function	V_{eff}/k_B (K)
He-He	
Chang and Cohen, Refs. 31 and 32	205
Massey and Woo, Ref. 33	126
Miller, Ref. 14	138,
He-H	
Miller, Ref. 14	37

the surface region is exactly the same as in the interior of the liquid. Until more accurate calculations of the Guyer-Miller type are available, we believe the present approximation to be a useful one. It has convincingly demonstrated that all three H isotopes are bound to the surface and with substantial binding energies, of the order of 1 K. This fact should be taken into account in designing and interpreting ultralow temperature experiments on spin-polarized hydrogen.

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