Interaction of Atomic Hydrogen with the Surface of Liquid ^{4}He

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The Euler-Lagrange equation for an impurity interacting with an inhomogeneous fluid is derived and applied to a description of the polarized hydrogen system, $\mathrm{H}_\uparrow$, $\mathrm{D}_\uparrow$, and $\mathrm{T}_\uparrow$ on the surface of liquid ^{4}He. We find well-defined, strongly bound physisorbed states for $\mathrm{T}_\uparrow$ and $\mathrm{D}_\uparrow$ and a weakly bound physisorbed state for $\mathrm{H}_\uparrow$.

Recently there has been a flourish of activity[1] centered on the possibility of laboratory studies of *atomic* hydrogen as a many-body system. This activity arises from the observation[2] that hydrogen atoms with their electron spins polarized, the $b^3\Sigma_u{}^+$ state, interact very weakly among themselves and that a weak interaction and small mass are the traditional recipe for a many-body system with quantum properties. Thus there is the expectation that the incredibly rich world of physics created by the helium isotopes would be further enriched if stable samples of the isotopes of spin-polarized hydrogen (hereafter, $\mathrm{H}_\uparrow$, $\mathrm{D}_\uparrow$, and $\mathrm{T}_\uparrow$ or collectively $\{\mathrm{H}_\uparrow\}$) could be prepared. The thrust of the initial round of experiments[1] is toward the development of a low-temperature (10^{-1} K) high-magnetic-field (10 T) sample space of high magnetic homogeneity that will maintain a polarized sample (i.e., a sample space designed to deter recombination to H_2 with the release of 5 eV). An important channel for $\mathrm{H}_\uparrow$ decay (H_2 production) will be spin-flip transitions during wall collisions.[3] An attractive possibility for shielding the $\mathrm{H}_\uparrow$ from the inevitable magnetic impurities in the walls is to coat the walls with a film of ^{4}He. Consequently we need to understand how $\{\mathrm{H}_\uparrow\}$ will behave in the presence of ^{4}He: Will $\{H_\uparrow\}$ mix into ^{4}He, bind in/on the surface of ^{4}He, or reside in the vapor?

In a study[4] which can be considered a precursor to this work, phase separation in bulk mixtures of $\{\mathrm{H}_\uparrow\}$ and ^{4}He were investigated. The zero-concentration chemical potential of $\mathrm{H}_\uparrow$, $\mathrm{D}_\uparrow$, and $\mathrm{T}_\uparrow$ in ^{4}He were calculated (see Table I) and it was found that, at $T=0$ K, $\mathrm{H}_\uparrow$ and $\mathrm{T}_\uparrow$ both *completely* phase separate from liquid ^{4}He. Even though the bulk mixtures will completely phase separate, $\{\mathrm{H}_\uparrow\}$ will be found preferentially in the vicinity of the ^{4}He *surface* due to the van der Waals interaction (i.e., in a physisorbed bound state). It is the description of this surface state which we shall discuss in this paper.

Lekner[5] has formulated a theory of the ^{3}He surface state on ^{4}He. In the $\{\mathrm{H}_\uparrow\}$-^{4}He systems the $\{\mathrm{H}_\uparrow\}$-^{4}He correlations are quite different from the ^{4}He-^{4}He correlations (the Lekner theory takes all correlations to be the same) so that a more general approach to the problem is called for. The generalization of Lekner's theory to the case of a nonisotopic impurity has been developed by Mantz and Edwards[6] for the case of $\{\mathrm{H}_\uparrow\}$ interacting with the ^{4}He surface. In this paper we derive and solve an Euler-Lagrange equation for the probability density of an impurity interacting with an inhomogeneous sample of ^{4}He. This formulation allows us to treat properly all two-particle correlations between the impurity atom and the ^{4}He.

We consider a system with $N-1$ He atoms and 1 impurity in a box of volume Ω such that N ^{4}He atoms fill the lower (negative-z) half-space with a Gibbs surface located at $z=0$. The Hamiltonian for the system can be written

$$H=-\frac{\hbar^2}{2m_\alpha}\nabla_\alpha{}^2+\sum_{j=1}^{N-1}V_{\alpha4}(r_{\alpha j})+H_4{}^{(N-1)}, \tag{1}$$

where the index α stands for the impurity, $V_{\alpha4}$ is the impurity-^{4}He interaction, and $H_4{}^{(N-1)}$ is the Hamiltonian for the $N-1$ ^{4}He atoms. Our approach is variational and we choose a trial func-

TABLE I. The zero-concentration chemical potential, μ_0, bound-state eigenvalue, ϵ_0, average position (with respect to a Gibbs surface at $z=0$), $\bar{z}$, and the rms spread about $\bar{z}$, Δz, for various atoms on a ^{4}He surface described by an Edwards-Fatouros density function, Eq. (8). The atom denoted Q is a fictitious mass-4 hydrogen.

Atom	μ_0 (K)	ϵ_0 (K)	$\bar{z}$ (Å)	Δz (Å)
^{3}He	-1.92	-2.61	-0.3	2.4
$\mathrm{H}_\uparrow$	$+37.5$	-0.10	$+13.5$	8.5
$\mathrm{D}_\uparrow$	$+9.94$	-1.11	$+4.8$	2.4
$\mathrm{T}_\uparrow$	$+0.65$	-2.42	$+2.8$	1.9
$Q_\uparrow$	-4.12	-4.12	Delocalized in bulk	

tion in the product form

$$\psi = \exp[\tfrac{1}{2} t_\alpha(z_\alpha)] \prod_{j=1}^{N-1} \exp[\tfrac{1}{2} u_{\alpha 4}(r_{\alpha j})] \prod_{j} \exp[\tfrac{1}{2} t_4(z_j)] \prod_{i<j} \exp[\tfrac{1}{2} u_{44}(r_{ij})], \tag{2}$$

where the two-particle factors $u_{\alpha 4}$ and u_{44} are chosen to depend only on relative scalar distance. Then the energy per unit area can be written

$$\frac{E}{A} = \frac{\hbar^2}{8m_\alpha}\int dz \, \frac{\rho_\alpha'(z)^2}{\rho_\alpha(z)} + \int\int dz_1 dz_2 \rho_\alpha(z_1)\rho_4(z_2)F_{\alpha 4}(z_1,z_2) + \frac{\hbar^2}{8m_4}\int dz \, \frac{\rho_4'(z)^2}{\rho_4(z)} + \tfrac{1}{2}\int\int dz_1 dz_2 \rho_4(z_1)\rho_4(z_2)F_{44}(z_1,z_2), \tag{3}$$

where $\rho(z)$ is the one-particle distribution function, the two-particle distribution functions have been decomposed into

$$\rho_{\alpha\beta}(1,2) = \rho_\alpha(z_1)\rho_\beta(z_2)g_{\alpha\beta}(\rho_{12},z_1,z_2) \tag{4}$$

and we have introduced the functions $F_{\alpha\beta}$,

$$F_{\alpha\beta}(z_1,z_2) = \int d^3\rho_{12}\, g_{\alpha\beta}(12)\tilde{v}_{\alpha\beta}(r_{12}) + \frac{\hbar^2}{4m_{\alpha\beta}}\frac{d}{dz_{12}}\left[\int d^3\rho_{12}\, g_{\alpha\beta}(12)\,\frac{z_{12}}{r_{12}}u_{\alpha\beta}'(r_{12})\right], \tag{5}$$

where

$$\tilde{v}_{\alpha\beta}(r_{12}) = v_{\alpha\beta}(r_{12}) - \frac{\hbar^2}{4m_{\alpha\beta}}\nabla^2 u_{\alpha\beta}(r_{12}),$$

and

$$\frac{1}{m_{\alpha\beta}} = \frac{1}{2}\left[\frac{1}{m_\alpha} + \frac{1}{m_\beta}\right].$$

The second term in Eq. (5) comes from the first Bogoliubov-Born-Green-Kirkwood-Yvon equation which, following Shih and Woo,[5] we have used to eliminate the wave functions t_α and t_4 in favor of the densities ρ_α and ρ_4. The bound-state energy which we wish to calculate is, like a chemical potential, a measure of the difference in energy of a system subsequent to changing one type of particle into the other. Thus the energy we need is the difference $(E-E_4)/A$, where E is given by (3) and E_4 is the energy of an N-particle ^{4}He system with a surface. From $\delta[(E-E_4)/A]/\delta\rho_\alpha(z)=0$ we find the (in general nonlinear) Schrödinger equation:

$$-\frac{\hbar^2}{2m_\alpha}\zeta_\nu''(z) + [\omega(z)+\tilde{\omega}(z)]\zeta_\nu(z) = \epsilon_\nu\zeta_\nu(z), \tag{6}$$

where $\rho_\zeta(z) \equiv \zeta^2(z)$ and the eigenvalue appears because of the number-conserving constraint $\int d^3r\, \zeta^2(z) = 1$. The potentials in (6) are defined by

$$\omega(z_1) = \frac{\hbar^2}{2m_4}\rho_4^{-1/2}\frac{d^2}{dz_1^2}(\rho_4^{1/2}) + \int dz_2\rho_4(z_2)[F_{\alpha 4}(z_{12}) - F_{44}(z_{12})], \tag{7}$$

and the $\tilde{\omega}$ term represents the contributions due to the $(\delta g_{\alpha\beta}/\delta\rho_\alpha)$ terms which we shall neglect. We have taken the $g_{\alpha\beta}(\rho_{12},z_1,z_2) \to g_{\alpha\beta}(r_{12})$, i.e., the *bulk* distribution functions [the $F_{\alpha\beta}$ in (7) depend only on z_{12} because our g's are chosen to be translationally invariant]. Here $\rho_4(z)$ is the density profile of a pure N-^{4}He system. This profile was chosen to be in Edwards-Fatouros[7] form

$$\rho_4(z)/\rho_0 = \{\exp[z/\xi + (l/z_0)^2(z/z_0)^2(1+z^2/z_0^2)^{-1}]+1\}^{-1}, \tag{8}$$

where $\rho_0 = 0.0172$ Å^{-3} is the ^{4}He zero-pressure bulk number density in the hypernetted-chain (HNC) approximation, the length $\xi \equiv \frac{1}{2}(\hbar^2/2m_4|E_4|)^{1/2} = 0.543$ Å and $E_4 = -5.13$ K is the bulk ^{4}He HNC energy, the length $l \equiv (\xi\rho_0\alpha 2m_4/\hbar^2)^{1/2} = 3.034$ Å and $\alpha = \frac{2}{3}\pi\epsilon_{44}\sigma_{44}^6$, where ϵ_{44} and σ_{44} are ^{4}He Lennard-Jones coefficients.[8] The parameter $z_0 = 2$ Å has been determined by minimizing the ^{4}He surface tension.[9] There are two points which should be noted about the Edwards-Fatouros function. (1) With the parameters ξ and l defined as above this function has the correct $z \to +\infty$ asymptotic (van der Waals) form (independent of z_0!). This feature is unimportant for a ^{3}He bound state which tends to dissolve into the bulk but it must be included in order to treat the $\{H_\uparrow\}$ bound states properly. (2) This form is number conserving (i.e., the Gibbs surface is at $z = 0$).

In Fig. 1 we show the densities and potentials for the cases of ^{3}He and $T_\uparrow$ adsorbed on the ^{4}He surface.[9] The comparison is of interest because the two impurities have the same mass and thus the differences in the physisorbed states is due entirely to the differences in the interactions (statistics plays no role since there is only one impurity atom). The ^{3}He atom sits in the surface with a preference for the ^{4}He bulk relative to the vacuum (because of the negative zero-concentration chemical potential). The bound-state energy -2.61 K (see Table I) is considerably higher than the experimental number (-5.1); nevertheless, the qualitative physics is correct: Our ^{3}He is bound preferentially in the surface relative to the bulk. [The major reason for the numerical discrepancy is the use of HNC $g(r)$'s.] The results for $T_\uparrow$ are qualitatively similar to those for ^{3}He. However, $T_\uparrow$ has a slightly positive zero-concentration chemical potential and thus it prefers the vacuum relative to the ^{4}He bulk; it sits on the surface. The potentials for both ^{3}He and $T_\uparrow$ have an interesting maximum in the surface region. In the ^{3}He case this structure is due to the asymmetry in $\rho_4(z)$ due to the presence of the z_0 term. Thus, in the Fermi-function, $z_0 \to \infty$, limit this structure disappears. The ^{3}He *eigenvalue* is insensitive to this structure because the probability density is peaked on the bulk side of the surface (in the Fermi-function limit, $\epsilon_0 = -2.41$ K). In the $T_\uparrow$ case, a large contribution to this structure comes from the cancellation between the potential energy difference term and the surface kinetic energy and thus in the Fermi-function limit the maximum remains. As shown in the figure, $T_\uparrow$ has a well-defined bound state ~ 2.8 Å off the ^{4}He surface with an rms spread, Δz, of only 1.9 Å. We also find one excited state with an energy of -0.26 K located 6.7 Å off the surface with an rms spread of 5 Å. Because $T_\uparrow$ prefers the vacuum side of the ^{4}He surface the Fermi-function limit differs considerably from the results obtained with the Edwards-Fatouros density function (e.g., in the Fermi-function limit the ground-state eigenvalue is raised to ~ -1.1 K).

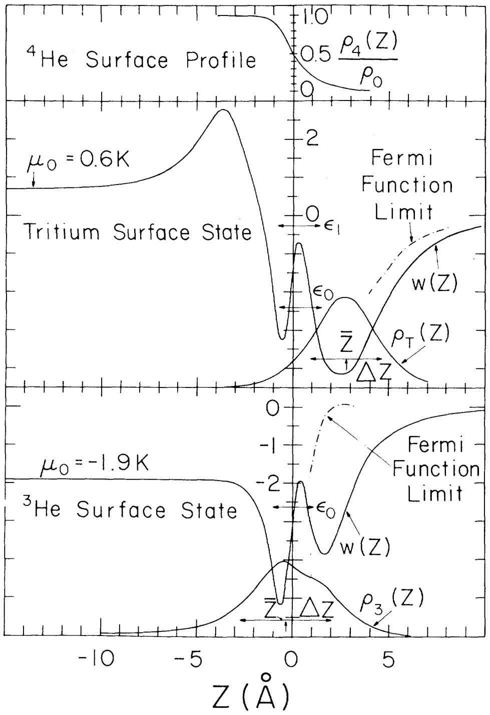

FIG. 1. The tritium, $T_\uparrow$, and ^{3}He surface states. The topmost part of the figure shows the ^{4}He surface profile in Edwards-Fatouros form as discussed in the text. For both $T_\uparrow$ and ^{3}He we show the effective single-particle potential, $\omega(z)$, and the probability density $\rho(z) = \zeta^2(z)$. The single-particle potentials go asymptotically to the bulk zero-concentration chemical potentials in the limit $z \to -\infty$. In the limit $z \to +\infty$ the potentials vanish with the correct van der Waals, $\sim z^{-3}$, form. The lower half of the figure shows that ^{3}He is bound preferentially in the surface with $\epsilon_0 + -2.6$ K, $\bar{z} \equiv \langle z \rangle = -0.3$ Å, and $\Delta z \equiv [\langle z^2 \rangle - \bar{z}^2]^{1/2} = 2.4$ Å. The upper half of the figure shows $T_\uparrow$ in a well-defined surface state with $\epsilon_0 = -2.42$ K, $\bar{z} = +2.8$ Å, and $\Delta z = 1.9$ Å. The dot-dashed lines indicate the $\rho_4(z) \to$ Fermi function limit for $\omega(z)$.

In Fig. 2 we show the surface states for $D_\uparrow$ and $H_\uparrow$. $D_\uparrow$ is quite strongly bound to the ^{4}He surface with a ground-state eigenvalue of -1.1 K) (if $D_\uparrow$ has a first excited state then the eigenvalue is smaller than 1 mK). The $D_\uparrow$ atom is well localized 4.8 Å off the surface with a rms spread of 2.4 Å. Finally, for the important $H_\uparrow$-^{4}He system, our calculations reveal a weak ($\epsilon_0 = -0.10$ K) bound state in which the $H_\uparrow$ resides some 13.5 Å above the surface with a spread of 8.5 Å. Because the $H_\uparrow$ atom is on average far from the surface, modifications of the calculation, to improve the ^{3}He bound-state energy, will not substantially change the characteristics of the $H_\uparrow$ bound state.

To summarize our conclusions, by use of an Euler-Lagrange approach, we have developed a theory to describe the interaction of an arbitrary

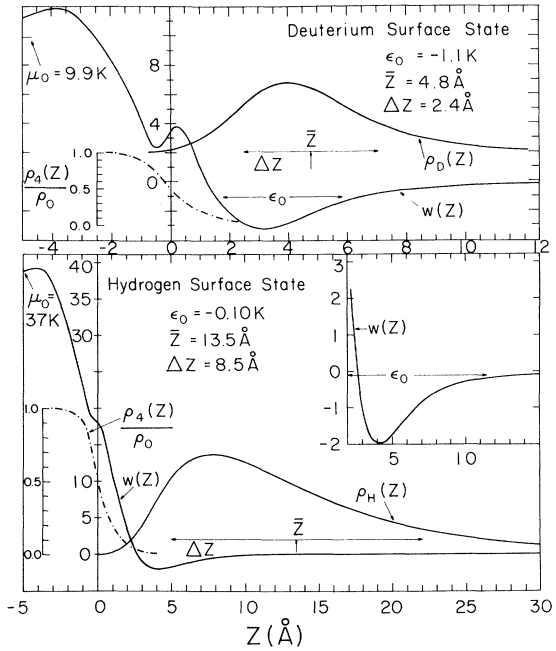

FIG. 2. The effective single-particle potentials, $\omega(z)$, and the probability densities, $\rho(z)=\xi^2(z)$, for hydrogen, $H_\uparrow$, and deuterium, $D_\uparrow$, on the ^{4}He surface. In the $z\to -\infty$ limit the potentials go asymptotically to the zero-concentration chemical potentials and in the $z\to+\infty$ limit the potnetials vanish with the correct, z^{-3}, van der Waals form. In both the top and bottom halves of the figure we indicate, with a dot-dashed line, the ^{4}He surface profile. The upper half of the figure shows the $D_\uparrow$ surface state fairly well localized 4.8 Å above the ^{4}He Gibbs surface. The lower half of the figure shows the $H_\uparrow$ surface state to be broad ($\Delta z = 8.5$ Å) and only weakly bound to the ^{4}He surface. In the inset we show the potential with the energy scale enlarged 5×. The inset shows the potential has a minimum $\simeq -2$ K at $z=4.15$ Å; in addition, we note that the potential passes through -0.1 K (the value of ϵ_0) at ~13.6 Å.

atom with the ^{4}He surface (we plan to apply this formalism to the electron-^{4}He system). We find well-defined physisorbed states for $T_\uparrow$ and $D_\uparrow$ (thus impurity $D_\uparrow$ in $H_\uparrow$ will be preferentially found on the walls). $H_\uparrow$ has a broad physisorbed state with an energy of -0.1 K. Because of phase-space considerations, this state will *not* be heavily populated for low-density systems.[10]

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[8] For the numerical work described here the potentials have been chosen in Lennard-Jones form with $\epsilon_{44}=10.22$ K, $\epsilon_{4\alpha}=6.57$ K, $\sigma_{44}=2.556$ Å, and $\sigma_{4\alpha}=3.19$ Å.

[9] The surface tension at 0.203 K Å^{-2} has a weak minimum around $z_0=2$ Å. In the limit $z_0\to+\infty$ (Fermi function) the surface tension is 0.21 K Å^{-2}.

[10] An additional problem might be any ^{3}He impurities in the ^{4}He since they would congregate on the surface.