

## Surface energy of liquid hydrogen with adsorbed helium

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The binding energy of helium to the surface of liquid hydrogen has been determined by measuring the surface energy of liquid hydrogen in the presence of helium gas. From the linear dependence of the surface energy on the density of helium gas the binding energy is found to be  $16 \pm 2$  K. The variation of the surface energy at higher densities cannot be explained in terms of simple extensions of a single-particle description of the binding of He to the  $H_2$  surface.

### I. INTRODUCTION

There has been interest recently in the properties of thin films of helium adsorbed on weak binding substrates. Cheng *et al.*<sup>1</sup> have predicted that the binding of helium to some materials may be too weak for helium to wet the surface. One substrate thought possibly to fall into this category is solid hydrogen. With an interest in the behavior of the first monolayer of helium on a weak binding substrate, there have been two recent studies of third sound in thin superfluid helium films on solid hydrogen.<sup>2,3</sup> The velocity of third sound can be used to determine the van der Waals force exerted on the film by the substrate. The values for the van der Waals constant found in the two measurements differ substantially, in one case, Ref. 2, being 4.6 K layer<sup>3</sup>, and in the other, Ref. 3, 21 K layer<sup>3</sup>. In an attempt to provide independent experimental information on the interaction of helium with condensed hydrogen we have measured the surface energy of liquid hydrogen in contact with helium gas. By studying the surface energy as a function of the gas density and temperature it is possible to determine the binding energy of helium atoms to the liquid hydrogen surface.

### II. EXPERIMENT

#### A. Apparatus

The dependence of the surface energy of liquid hydrogen on helium gas density was measured by the capillary-rise technique.<sup>4</sup> By measuring the heights,  $h_1$  and  $h_2$ , of the liquid in two capillaries of radii  $r_1$  and  $r_2$  the surface energy can be determined from

$$\sigma = \frac{\Delta\rho g r_1 r_2}{2(r_1 - r_2)} \left[ (h_1 - h_2) - \frac{(r_1 - r_2)}{3} \right], \quad (1)$$

where  $\Delta\rho$  is the difference in density between the liquid and the gas phases and  $g$  is the acceleration due to gravity. Complete wetting of the glass capillaries by the hydrogen is assumed.

A schematic of the apparatus used for the measurements is shown in Fig. 1. The experiment was performed using two precision-bore capillaries of radii  $0.0229 \pm 0.0003$  and  $0.0982 \pm 0.0003$  cm of 12 cm length

held vertically inside a heavy wall Pyrex tube of inner diameter 2.4 cm and outer diameter 3.2 cm. The cylinder was capped by copper end plates using indium as a sealant between the copper and glass. The assembly was held together by six stainless steel rods loaded in tension and capable of withstanding pressures in the cylinder of up to 60 atm without leaking. To maintain a uniform

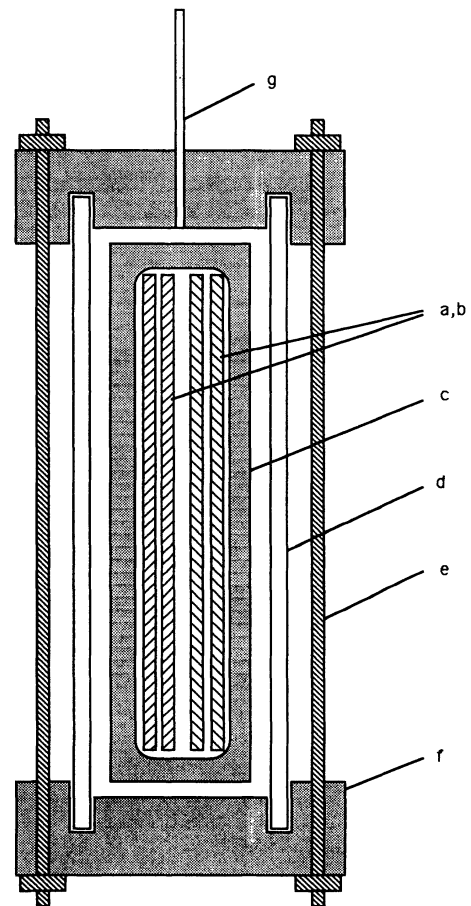


FIG. 1. Schematic diagram of the cell. (a) and (b) Two glass capillaries. (c) Copper inner sleeve. (d) Pyrex tube. (e) Steel rod. (f) End cap. (g) Gas inlet tube. Not shown: outer copper sleeve.

temperature along the capillaries a cylindrical copper sleeve, with a slit for viewing the capillaries, was placed inside the Pyrex tube. A much heavier piece of copper surrounded the whole assembly, also for the purpose of assuring temperature uniformity.

The apparatus was placed in a glass Dewar and cooled by the gas evaporated from a bath of liquid helium at the bottom of the Dewar. A thermometer and heater were attached on each copper end plate and the temperatures of the plates were independently regulated to be constant and the same to within 0.02 K during a measurement. It was estimated that the temperature in the cell was uniform to within 0.02 K. Hydrogen and helium gas were admitted into the cell through a tube into the top end cap. The gases were passed through a filter at 20 K of 0.01  $\mu\text{m}$  alumina powder to remove contaminants by adsorption. Also, a catalyst (Apachi nickel-silica gel) converted the hydrogen to the equilibrium para form at 20 K. A separate tube, unimpeded by filter and catalyst, was used to measure the pressure in the cell. The height of the liquid in the capillaries was measured using a long objective microscope with video camera attachment.

To obtain the surface energy from Eq. (1), knowledge is required of the density of the gas and of the liquid as a function of temperature and pressure. This is made somewhat more complicated and uncertain by the changing concentration of hydrogen in the predominantly helium vapor phase and of helium in the predominantly hydrogen liquid phase. Publications from the National Bureau of Standards were used to obtain the density of helium gas,<sup>5</sup> and hydrogen liquid<sup>6</sup> as a function of pressure. Studies of mixtures of hydrogen and helium have been reported in a number of papers, the data of Street *et al.*<sup>7</sup> on the concentrations of He and H<sub>2</sub> in the two phases down to 15 K and up to 30 atm being the most relevant to the present measurements. Small concentrations of the minor constituent in a phase can have a substantial influence of the computed surface energy when the pressure approaches the barotropic condition, i.e., when the densities of the gas and liquid phases are equal.<sup>8,9</sup> For that reason the measurements used in the analysis here only extend up to a gas density of 0.04 g/cm<sup>3</sup>. Observations were made at higher pressures, even above the barotropic point where the phases are inverted and the liquid is at the top of the cell, but because of possible large systematic errors the results are not reported here.

The problem associated with the variation in concentrations of the constituents in the two phases is further complicated by the time required to establish equilibrium. Since the coefficient for diffusion of He in liquid H<sub>2</sub> is most likely between 10<sup>-4</sup> and 10<sup>-5</sup> cm<sup>2</sup>/sec,<sup>10</sup> the time for the helium to diffuse several cm in the small capillary could be up to a day. Rather than try to establish equilibrium concentrations we chose to perform measurements in a much shorter time, taking 10 min or less to establish thermal equilibrium at a particular temperature and pressure. In analyzing the data it was then assumed that there was no He in the liquid. However, in the gas the equilibrium concentration of H<sub>2</sub> and He were assumed to exist due to the higher diffusion coefficient and

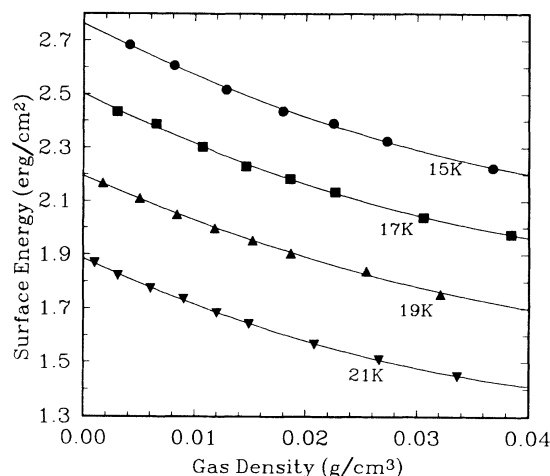


FIG. 2. Surface energy of liquid hydrogen as a function of helium gas density at several temperatures.

the probability of convection during a change of pressure and gas density in the cell. Possibly systematic errors introduced by these assumptions are discussed below.

## B. Results

The results for the dependence of the surface energy of liquid hydrogen on the density of helium gas above it are shown in Fig. 2. A least-squares fit of the data points to the equation

$$\sigma = \sigma_0 + a_1\rho + a_2\rho^2 \quad (2)$$

yields the values listed in Table I for the coefficients at four different temperatures.

The values obtained for  $\sigma_0$  are within 3% of the published values<sup>11,12</sup> for the surface energy of liquid hydrogen in equilibrium with its saturated vapor.

## III. DISCUSSION

### A. Linear approximation

The simplest model by which to describe the behavior of the surface energy of liquid hydrogen under the influence of adsorbed helium atoms is to assume that helium on the surface forms a two-dimensional ideal gas, the binding of an atom to the surface being characterized by a single state with energy  $\epsilon_0$  below that in the vapor. The change in surface energy of the liquid as a consequence of the adsorption in such a model can be expressed in terms

TABLE I. Coefficients of Eq. (2) at several different temperatures.

$T$ (K)	$\sigma_0$ (erg/cm <sup>2</sup> )	$a_1$ (erg cm/g)	$a_2$ (erg cm <sup>4</sup> /g <sup>2</sup> )
15	2.76	-20.9	170
17	2.50	-20.2	170
19	2.20	-18.1	140
21	1.88	-18.8	170

of the surface density of helium atoms,  $n_s$ , and is given simply by

$$(\Delta\sigma)_1 = -n_s kT. \quad (3)$$

Such an expression was obtained by Edwards *et al.*<sup>13</sup> in considering the change in free energy of the surface of liquid  $^4\text{He}$  due to the presence of adsorbed  $^3\text{He}$ . The system of  $^3\text{He}$  on the surface of  $^4\text{He}$  is analogous to that being considered here except for the change in statistics, unimportant at low surface densities. A more general derivation of Eq. (3) can be found in Landau and Lifshitz<sup>14</sup> for the change in free energy of the surface of a liquid when the chemical potential of the adsorbing species in a reservoir in equilibrium with the surface is proportional to  $kT \ln n$ ,  $n$  being the density in the reservoir. This condition certainly holds for helium adsorbing on hydrogen when the helium gas density is low.

To obtain the change in surface energy in terms of measurable quantities, the number density,  $n_s$ , of helium atoms on the surface is related to the number density,  $n_g$ , in the gas phase by equating their chemical potentials. The chemical potential for helium on the surface,  $\mu_s$ , is taken at low densities to be

$$\mu_s = -\varepsilon_0 + \mu^*, \quad (4)$$

where  $\mu^*$  is the chemical potential of an ideal two-dimensional gas of helium atoms on the surface. The relationship between  $\mu^*$  and  $n_s$  is taken to be

$$\mu^* = kT \ln(\lambda_s^2 n_s), \quad (5)$$

where the thermal wavelength associated with motion on the surface allows for the possibility that the effective mass may be different than the free mass of a helium atom; i.e.,  $\lambda_s = (h^2/2\pi m^* kT)^{1/2}$ .

The chemical potential in the gas is

$$\mu_g = kT \ln(\lambda_g^3 n_g). \quad (6)$$

With  $\mu_s = \mu_g$  the above expressions can be combined to yield

$$(\Delta\sigma)_1 = -\frac{hk^{1/2}}{(2\pi)^{1/2} m^{3/2}} \left[ \frac{m^*}{m} \right] T^{1/2} e^{\varepsilon_0/kT} n_g, \quad (7)$$

or in terms of the mass density,  $\rho$ , of the gas

$$(\Delta\sigma)_1 = -1.80 \left[ \frac{m^*}{m} \right] T^{1/2} e^{\varepsilon_0/kT} \rho. \quad (8)$$

Equation (8) can be compared to the  $a_1\rho$  term of Eq. (2) to determine the values of the binding energy and the effective mass on the surface. The best statistical fit of the data in Table I yields

$$\frac{m^*}{m} = 1.05 \pm 0.15, \quad \text{and} \quad \varepsilon_0/k = 15.7 \pm 2.7 \text{ K}. \quad (9)$$

If  $m^*/m$  is set equal to 1, then the best value for  $\varepsilon_0/k$  is  $16.7 \pm 1.0$  K. The errors represent only the standard deviation of the statistical fit to the data. Since the possible systematic errors in the measured surface energy resulting from inaccuracies in the concentrations of He and  $\text{H}_2$

in the two phases can only become significant at large densities and the calculated value of  $\varepsilon_0$  is most sensitive to the results at low densities, the error that could be introduced into  $\varepsilon_0$  is estimated to be no more than 5%.

## B. Quadratic terms

There are several different effects that can possibly contribute to a nonlinear dependence of the surface energy on gas density. These are discussed separately below.

### 1. Surface interactions

Edwards *et al.*,<sup>13</sup> in calculating the dependence of the surface free energy, went beyond terms linear in the density and included the possibility of interactions on the surface among pairs of adsorbed atoms. If the energy of interaction of an atom with other atoms on the surface is taken as  $n_s v_0$ , the chemical potential on the surface contains an additional term and is modified from Eq. (4) to be

$$\mu_s = -\varepsilon_0 + \mu^* + n_s v_0, \quad (10)$$

and the change in surface free energy becomes

$$\Delta\sigma = -n_s kT - \frac{1}{2} n_s^2 v_0. \quad (11)$$

When  $\Delta\sigma$  is now expressed in terms of mass density,  $\rho$ , it contains terms in  $\rho^2$  arising from several different sources, one directly from the second term on the right side of Eq. (11) and another from the first term in Eq. (11) when combined with the additional dependence of  $\mu_s$  on  $n_s$  in Eq. (10). Furthermore, there are small corrections, also of order  $\rho^2$ , which result from the use of quantum statistics in relating chemical potential and density both for the two-dimensional gas on the surface and the gas phase. Equations (5) and (6) are expressions based on classical statistics valid in the low density limit. When all these factors are taken into account the quadratic dependence of the surface energy becomes

$$(\Delta\sigma)_{2s} = 1.2 \times 10^{16} \frac{1}{T} e^{2\varepsilon_0/kT} \times \left[ \frac{v_0}{k} - 3.8 \times 10^{-15} (1 - \sqrt{2} e^{-\varepsilon_0/kT}) \right] \rho^2. \quad (12)$$

In obtaining Eq. (12)  $m^*/m$  was set equal to 1.

For interaction of atoms on the surface to be the origin of the quadratic dependence of  $\Delta\sigma$ , the required value of  $v_0$ , obtained by equating the  $a_2\rho^2$  term of Eq. (2) to  $(\Delta\sigma)_{2s}$  of Eq. (12), is found to be

$$v_0 = (6 \pm 2) \times 10^{-30} \text{ erg/cm}^2. \quad (13)$$

Since  $v_0$  is found to be positive, the helium interactions on the surface would have to be repulsive. Inaccuracies in the concentrations of the constituents in both the liquid and the gas can introduce large systematic errors in  $a_2$  and the calculated value of  $v_0$ , as much as 30%. The magnitude of the calculated interaction energy looks unreasonably large, given that it is repulsive. Whitlock

*et al.*<sup>15</sup> predict at zero temperature a two-dimensional helium gas would condense to a liquid phase with a density of  $4.5 \times 10^{14} \text{ cm}^{-2}$ .

### 2. Interactions in the gas

The nonideality of helium in the gas phase can make a contribution to the quadratic dependence of the surface energy on density. The density of helium gas is somewhat higher at low pressures than predicted by the ideal gas law. In the spirit of the formulation above, this deviation from ideality can be expressed as a correction to the chemical potential-density relation for the gas, i.e., the right side of Eq. (6) can be modified to include a higher order term in the density. Following the discussion of Huang<sup>16</sup> of an imperfect Bose gas, one can show that the deviation of the pressure from the ideal gas law at high temperatures can be written as  $\delta p = \beta \rho^2$  where  $\beta$  is a measure of the size of the interaction between atoms in the gas. Similarly, the correction to the chemical potential can be written as  $n_g v_1$ , where  $v_1 = 2m^2\beta$ , so that Eq. (6) becomes

$$\mu_g = kT \ln(\lambda_g^3 n_g) + n_g v_1. \quad (14)$$

When this correction term is carried through to the change in surface energy it gives rise to an additional contribution to  $\Delta\sigma$  of magnitude

$$(\Delta\sigma)_{2g} = -2\beta\lambda e^{\epsilon_0/kT} \rho^2. \quad (15)$$

Again,  $m^*/m$  has been set equal to unity. The value of  $\beta$  obtained from the measured density variation with pressure<sup>5</sup> depends on temperature, varying between  $-2 \times 10^8$  and  $-7 \times 10^8 \text{ erg cm}^3/\text{g}^2$  for temperatures between 21 and 15 K. This translates into a contribution of up to 40% to the magnitude of the experimental value of  $a_2\rho^2$  in Eq. (2) at 15 K, but much less at higher temperatures. Interactions in the gas may make some contribution to the second order density variation of the surface energy, but the effect is not large.

### 3. Effect of gas on binding energy

The gas, by interacting with the atoms on the surface, can produce a quadratic density dependence of the surface energy in another manner. The binding energy of an atom to the surface is the result of the van der Waals attraction of the surface atom to the substrate. But in this system there is also a van der Waals attraction of a surface to the gas. Thus, as the gas density increases, the effective potential for a He atom near the surface changes and the binding energy decreases.

The magnitude of this effect can be estimated as follows. The ratio of the van der Waals potential for He gas occupying a half space to that of liquid  $\text{H}_2$  is

$$\frac{\alpha_{\text{He}} \rho_{\text{He}}/m_{\text{He}}}{\alpha_{\text{H}_2} \rho_{\text{H}_2}/m_{\text{H}_2}},$$

where the  $\alpha$ 's and  $m$ 's are the polarizabilities and masses of the respective molecules, and  $\rho_{\text{H}_2}$  is the liquid  $\text{H}_2$  density. On substitution for the known quantities this ratio

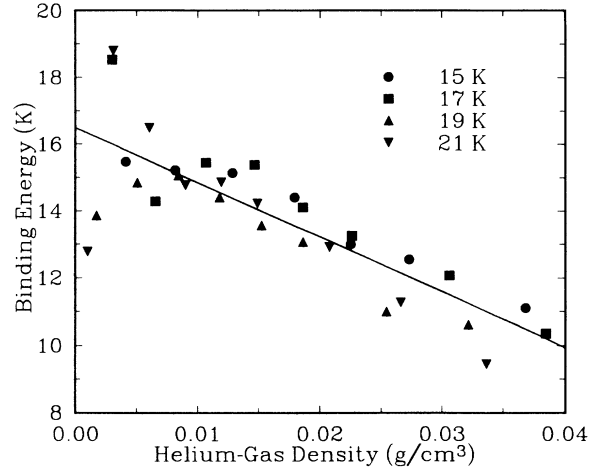


FIG. 3. Dependence of the binding energy of helium to the surface of liquid hydrogen assuming the nonlinear variation of surface energy is explained by a density dependent binding energy. The line is the best fit to the data;  $\epsilon = 16.5k(1 - 10\rho)$ .

is found in terms of the He gas density,  $\rho$ , to be  $1.5\rho$ . If one assumes that the attraction of He to the surface is reduced by this ratio and further assumes that the binding energy is proportional to the attractive part of the potential,<sup>17</sup> then the density dependence of the binding energy becomes

$$\epsilon = \epsilon_0(1 - 1.5\rho). \quad (16)$$

The experimental results illustrated in Fig. 2 can be analyzed in terms of a density dependent binding energy by replacing  $\epsilon_0$  in Eq. (8) by  $\epsilon$  and relating that expression to the total change in surface energy in Eq. (2). A plot of the density dependence of  $\epsilon$  found in this way is illustrated in Fig. 3. The best linear fit to the data, with  $m^*/m = 1$ , is

$$\epsilon = 16.5k(1 - 10\rho); \quad (17)$$

hence the measured dependence is a factor of 7 larger than expected from a crude estimate.

### 4. Density change of the liquid

The increase in density of the liquid with pressure will produce a change in the binding energy of a helium atom to the surface. However, the sign of the change in  $\epsilon_0$  produced by this effect is opposite to that required to explain the measured quadratic dependence of surface energy. While of the correct sign, the variation in  $\sigma$  produced by the change in concentration of He in the liquid is very small.

## IV. CONCLUSIONS

The model of helium adsorbed on the surface of liquid hydrogen in which the He forms a two-dimensional gas with a binding energy to the surface of 16 K per atom and an effective mass approximately that of the free atom fits well the dependence of the surface energy on helium

gas density at low densities. While the binding energy and the van der Waals constant are not the same quantity, the value of 16 K determined for the binding energy is consistent with the result that the van der Waals constant for He on solid H<sub>2</sub> is 21 K layer<sup>3,3</sup>.

The model used to characterize the linear dependence of the surface energy needs clarification and possibly extension in one respect. Pierre *et al.*<sup>18</sup> in studying the adsorption of He on solid H<sub>2</sub> found, in addition to a bound state on the surface with an energy of approximately 15 K, an excited state with energy 2 K below the continuum. If the statistical thermodynamics discussed above were modified to include the possibility of such an excited state, then the experimental results cannot be reconciled in a plausible manner with predictions of the model. One possible explanation may be that while an isolated helium atom bound to a hydrogen surface may possess an excited state, the interactions of surface atoms with atoms in the high density gas are so large at temperatures of order 20

K that the system cannot be characterized in such a manner.

The strong nonlinear dependence of surface energy on density at high gas pressures could be due to any of several effects that go beyond the single-particle model of atoms adsorbed on the surface. Without a more quantitative calculation describing these cooperative effects one cannot determine the correct explanation of experimental observations when the density of the gas becomes large.

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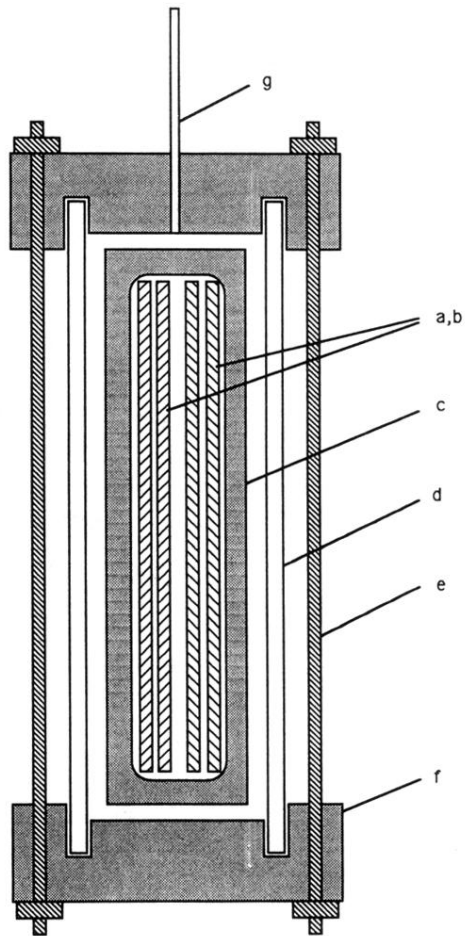


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