Second virial coefficient of helium adsorbed on liquid hydrogen

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The nonlinear dependence of the surface energy of liquid hydrogen as a function of the density of helium gas in equilibrium with the liquid surface has been used to determine the second virial coefficient of the two-dimensional gas of helium atoms adsorbed on the surface. The surface energy of both liquid hydrogen and liquid deuterium has been measured in the presence of ^{4}He and ^{3}He. The experimental results are in rough agreement with theoretical prediction.

I. INTRODUCTION

Recent interest in the properties of helium on the surface of weak binding substrates[1] has led us to study the behavior of helium adsorbed on liquid hydrogen. The change in surface energy of the liquid can be used to measure the density of adsorbed atoms,[2] and from such measurements the binding energy of the adsorbed atoms to the surface and the interaction among atoms on the surface can be determined. Measurements of the binding energy of helium on liquid hydrogen have been reported previously.[3,4] We discuss below the interaction among helium atoms adsorbed on the liquid surface in terms of a second virial coefficient for a two-dimensional gas. This analysis of the interactions among atoms can be related to the theoretical treatment of a low-density helium monolayer as a two-dimensional imperfect gas.

II. EXPERIMENT

The dependence of the surface energy of liquid hydrogen on helium gas density was measured by the capillary rise technique. 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

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

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

Four binary systems were studied—^{4}He and ^{3}He adsorbed on the surface of liquid hydrogen and liquid deuterium. The H_2 and D_2 were converted to their low-temperature equilibrium orthopara ratios using a magnetic catalyst. Two different cells were used, one for ^{4}He and the other with much smaller gas volume at low temperatures for ^{3}He. Further details of the apparatus can be found in Ref. 5.

To obtain the surface energy from Eq. (1), knowledge is required of the density of the gas and the liquid as a function of temperature and pressure. This is made somewhat complicated by the changing concentration of hy-drogen in the predominantly helium vapor phase, and of helium in the predominantly hydrogen liquid phase. Small concentrations of the minor constituent in a phase can have a substantial influence on the computed surface tension when the barotropic condition is approached, i.e., when the densities of the liquid and vapor are equal. Several papers have reported studies of mixtures of helium and hydrogen isotopes, the data of Hiza[6] on the concentration of each component in the two phases for temperatures between the hydrogen triple point and the critical point and for pressures up to 30 atm being the most relevant to the present measurements. Observations were made at pressures above the barotropic point, where the phases are inverted with the liquid above the more dense vapor. However, the increasing uncertainty in the density and composition of the vapor at higher pressure limits the usefulness of such measurements, and the data reported here are restricted to pressures below 25 atm.

The temperature and pressure dependence of the density of the vapor phase was analyzed using the virial expansion

$$P = nkT[1 + B(T)n + C(T)n^2 + D(T)n^3 + \cdots],\qquad(2)$$

where n is the number density of molecules in the gas, and $B(T)$, $C(T)$, and $D(T)$ are the virial coefficients. For a gas of two molecular species, the virial coefficients take the form

$$B(T) = B_{ii}x_i^2 + 2B_{ij}x_i x_j + B_{jj}x_j^2,\qquad(3)$$

$$C(T) = C_{iii}x_i^3 + 3C_{iij}x_i^2 x_j + 3C_{ijj}x_i x_j^2 + C_{jjj}x_j^3,\qquad(4)$$

where x_i and x_j are the mole fractions of the two species helium and hydrogen, respectively, in the mixture. A discussion of the values of the virial coefficients used in the analysis can be found in the Appendix.

The determination of the helium gas density from the equation of state made use of the measurements of Hiza[6] to determine the ratio of hydrogen to helium in the vapor as a function of pressure.

The composition of the liquid phase presents a different problem from that of the vapor. While the equilibrium composition of the liquid as a function of pressure is known with sufficient accuracy,[6] the time required to establish equilibrium by diffusion of the helium in the hy-

drogen is very long due to the geometry of the cell and capillaries. Consequently, the measurements were performed on time scales that were very short compared to equilibration times in the liquid, but long for equilibration in the gas. For the purpose of computing the density, the liquid was assumed to be pure hydrogen at the corresponding pressure.[7,8]

III. RESULTS

The surface energy of liquid hydrogen at a given temperature is expressed as a function of helium gas density n_{ig} by the relation

$$\sigma = \sigma_0 + \alpha_1 n_{ig} + \alpha_2 n_{ig}^2 . \tag{5}$$

A typical set of data is illustrated in Fig. 1, and the experimentally determined coefficients of Eq. (5) are listed in Table I for the various systems. The values of the surface energy of pure hydrogen and deuterium as measured previously[9-11] are listed for comparison with the present measurement σ_0. In general, there is good agreement between the present measurements of the surface energy of pure H_2 and D_2 and the results of previous work. At most temperatures the difference is within 1%. Only in a few cases do the results differ by as much as 3%.

As a model for the system we take the vapor to be an interacting gas of helium atoms with a minor concentration of H_2, and consider helium atoms adsorbed on the liquid hydrogen to be an interacting two-dimensional gas, the binding energy to the surface being ϵ_0 per atom. The He in the vapor has a chemical potential given by

$$\mu_g = kT \ln(\lambda^3 n_{ig}) + 2kT(n_{ig}B_{ii} + n_{jg}B_{ij}) . \tag{6}$$

where $\lambda = (2\pi\hbar^2/mkT)^{1/2}$ is the thermal wavelength. The subscripts i and j represent helium and hydrogen, respectively. In what follows we neglect the small n_{jg} term, since the accuracy of the data does not warrant its inclusion. Equation (6) is the standard expression for the chemical potential of an interacting three-dimensional (3D) gas in the context of the virial expansion to order n^2.
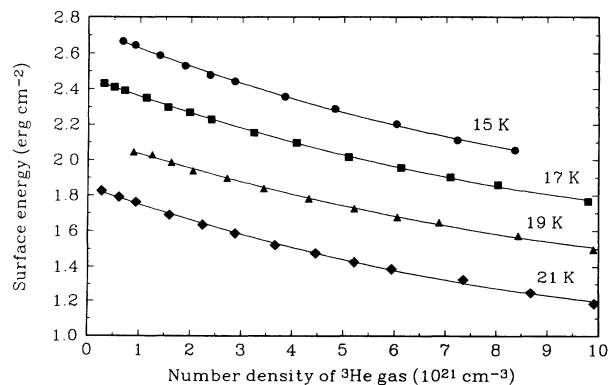
A two-dimensional gas of atoms interacting with one

FIG. 1. Surface energy of liquid H_2 as a function of ^{3}He gas density at several temperatures. The curves drawn through the data points are least-squares fits to the data according to Eq. (5).

TABLE I. Coefficients of Eq. (5).

	T K	σ_0^a erg cm^{-2}	σ_0^b erg cm^{-2}	α_1 erg cm $\times 10^{22}$	α_2 erg cu^4 $\times 10^{45}$
^{3}He/H_2	15.0	2.81	2.74	−1.13	3.8
	17.0	2.48	2.46	−1.04	3.5
	19.0	2.16	2.13	−0.97	2.9
	21.0	1.83	1.84	−0.91	3.2
^{4}He/H_2	15.0	2.81	2.76	−1.27	5.4
	17.0	2.48	2.48	−1.21	5.4
	19.0	2.16	2.19	−1.14	3.7
	21.0	1.83	1.87	−1.11	3.0
^{3}He/D_2	20.0	3.54	3.58	−1.17	1.4
	21.0	3.32	3.32	−1.22	3.6
	22.0	3.10	3.10	−1.27	4.3
	23.0	2.88	2.99	−1.33	4.4
	24.0	2.67	2.77	−1.26	4.1
^{4}He/D_2	20.0	3.54	3.55	−1.69	6.0
	21.0	3.32	3.31	−1.61	6.1
	22.0	3.10	3.08	−1.58	4.5
	23.0	2.88	2.91	−1.37	5.4
	24.0	2.67	2.71	−1.48	4.6
	26.0	2.23	2.24	−1.48	5.1

[a]From Refs. 9–11.
[b]Present measurement.

another in the plane has to order N^2 in a virial expansion a free energy given by[12]

$$F_{2D} = N_s kT[\ln(\lambda^2 N_s/A) - 1] + N_s^2 kTB_s/A . \tag{7}$$

N_s is the total number of helium atoms adsorbed on the surface of area A, and B_s is the surface second virial coefficient. To describe He atoms adsorbed on the surface of liquid H_2, we must add the term $-\epsilon_0 N_s$ to account for the binding energy. Furthermore, the surface atoms interact with atoms in the vapor, and have their free energy modified correspondingly. The interaction between surface and vapor atoms is approximated by $N_s(N_g/V)B_{ii}$. This expression is obtained by assuming that the surface atoms interact with the vapor atoms in the half-space above the surface, the spatial distribution of atoms in the vapor being unaffected by the presence of the surface. Hence the second virial coefficient for the vapor, B_{ii}, appears in the interaction. The free energy of the adsorbed atoms is then

$$F_{ads} = F_{2D} - \epsilon_0 N_s + N_s \left[\frac{N_g}{V} \right] B_{ii} ,$$

or

$$F_{ads} = -\epsilon_0 N_s + N_s kT[\ln(\lambda^2 N_s/A) - 1]$$
$$+ N_s^2 kTB_s/A + N_s \left[\frac{N_g}{V} \right] B_{ii} . \tag{8}$$

Various thermodynamic parameters of the surface atoms may now be computed. The chemical potential is

$$\mu_s = \left[\frac{\partial F_{ads}}{\partial N_s}\right]_{T,A}$$

$$= -\epsilon_0 + kT \ln(\lambda^2 n_s) + 2kTn_s B_s + kTn_g B_{ii} , \quad (9)$$

where $n_s = N_s/A$. The effect of the interaction between surface and vapor atoms can be ignored in the expression for the free energy or chemical potential of the vapor because of the very different magnitudes of N_s and $N_g = n_g V$. The change in surface energy, related to the spreading pressure, is

$$\sigma - \sigma_0 = -p_s = \left[\frac{\partial F_{ads}}{\partial A}\right]_{T,N_s} = -n_s kT - n_s^2 kT B_s . \quad (10)$$

By equating the chemical potentials μ_s [Eq. (9)] and μ_g [Eq. (6)], n_s can be determined as a function of n_g. The change in surface energy Eq. (10) can be expressed in terms of the He gas density. Comparing to Eq. (5), we find

$$\alpha_1 = -kT\lambda e^{\epsilon_0/kT} \quad (11)$$

and

$$\alpha_2 = -kT\lambda e^{\epsilon_0/kT}(B_{ii} - B_s \lambda e^{\epsilon_0/kT}) . \quad (12)$$

The values of the binding energy, ϵ_0, obtained from Eq. (11) and the measurement of α_1 can be found in Table II. Implicit in the calculations is the assumption that the effective mass of a helium atom adsorbed on the surface is the same as the mass of an atom in the gas. If this assumption is removed and the effective mass on the surface is treated as a variable to be determined along with the adsorption energy from the experimental data, the

TABLE II. Binding energies of helium on hydrogen.

	ϵ_0/k K
^{3}He/H$_2$	9.6
^{3}He/D$_2$	14.5
^{4}He/H$_2$	15.0
^{4}He/D$_2$	22.3

mass in all cases is found to be slightly larger than the free mass (from 2 to 14% larger), but not by a statistically significant amount given the errors in the measurements. The binding energies listed in Table II differ slightly from those given earlier,[4] which resulted from a preliminary analysis of the data. The estimated uncertainties in the binding energies are ±2 K for ^{3}He and ±1 for ^{4}He.

The experimental results for the binding energies are consistent with one another to the extent that for a given substrate ^{4}He is more strongly bound than is ^{3}He. Also, a given helium isotope is more strongly bound to D$_2$ than to H$_2$, liquid deuterium having a molar density 20% larger than liquid hydrogen. While we are unaware of any theoretical calculations of the binding of helium to the surface of liquid hydrogen, there are estimates of the adsorption of helium on solid hydrogen.[13,14] The theoretical results of Pierre, Guignes, and Lhullier[13] are roughly consistent with the present measurements of the liquid, the calculated adsorption energy for helium on hydrogen lying between 10 and 20 K, depending on the isotope, crystal surface, form assumed for the interaction, etc. The recent Monte Carlo calculations of Wagner and Ceperley[14] for the binding energy of ^{4}He on solid H$_2$ give a value of 16 K in the limit of low-He surface coverage.

TABLE III. Virial coefficients used in the analysis of binary mixtures of helium and hydrogen.

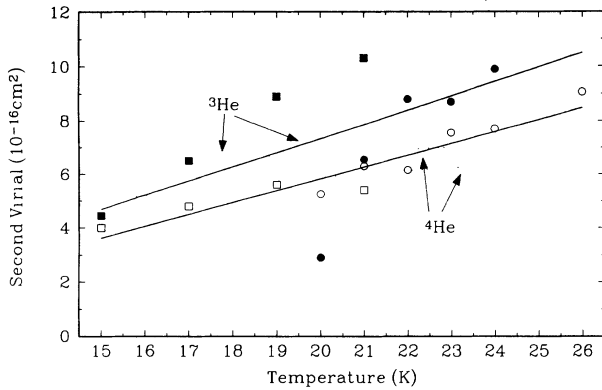|	T K	b_{ii} cm^3 mole^{-1}	b_{ij} cm^3 mole^{-1}	b_{jj} cm^3 mole^{-1}	c_{iii} cm^6 mole^{-2}	c_{iij} cm^6 mole^{-2}	d_{iiii} cm^9 mole^{-3}
^{3}He/H$_2$	15.0	−5.36	−26	−220	290	900	2900
	17.0	−2.81	−17	−180	270	780	2600
	19.0	−0.78	−9	−160	250	700	2300
	21.0	+0.86	−8	−140	230	640	2100
^{4}He/H$_2$	15.0	−10.7	−33	−220	400	720	4600
	17.0	−7.2	−25	−180	360	630	3900
	19.0	−5.0	−19	−160	340	570	3600
	21.0	−2.6	−15	−140	340	520	3600
^{3}He/D$_2$	20.0	+0.07	−10	−160	240	640	2200
	21.0	+0.85	−10	−150	230	610	2100
	22.0	+1.57	−9	−140	230	590	2000
	23.0	+2.22	−9	−140	220	570	1900
	24.0	+2.81	−9	−130	220	550	1900
^{4}He/D$_2$	20.0	−3.80	−19	−160	340	520	3600
	21.0	−2.60	−15	−150	320	500	3200
	22.0	−1.40	−10	−140	290	480	2800
	23.0	−0.70	−8	−140	280	470	2700
	24.0	+0.02	−5	−130	270	450	2600
	26.0	+1.70	−3	−120	250	430	2300

FIG. 2. The two-dimensional second virial coefficient of helium adsorbed on hydrogen. The dotted lines are the results of the theoretical calculations of Siddon and Schick (Ref. 15). The solid lines are a guide to the eye for the experimental results. Experimental results: solid squares ^{3}He on H_2; solid circles ^{3}He on D_2; open squares ^{4}He on H_2; and open circles ^{4}He on D_2.

In these calculations Wagner and Ceperley allow for the possibility that the H_2 molecules in the surface layer may adjust their positions in the presence of an adsorbed He atom. Hence their results may be a better approximation of the case of He adsorbed on the liquid surface than one would otherwise expect. In addition, they find that at low temperatures the binding energy depends on He surface coverage, increasing in magnitude even in the low submonolayer range. This is presumably due to the long-range attractive interaction between He atoms on the surface. Such an effect should be negligible at the much higher temperatures of the present measurements for the same reason that the second virial coefficient changes from being large negative at low temperatures to being small positive above 24 K for ^{4}He (see Table III). In the present analysis the density dependence of the binding energy is described in terms of a surface second virial coefficient.

The values of the second virial coefficient for a two-dimensional gas of helium atoms, B_s, calculated using Eq. (12) and the measured dependence of the surface energy on density, can be found in Fig. 2. The solid lines drawn to guide the eye are the best linear fits to the results for ^{3}He and ^{4}He separately. The experimental results for ^{3}He can be seen to scatter more than those for ^{4}He for the reasons discussed earlier. The dotted lines plotted in Fig. 2 are the theoretical results of Siddon and Schick,[15] who have calculated the second virial for a two-dimensional gas of both ^{4}He and ^{3}He using a Lennard-Jones 6-12 potential to represent the interaction between two helium atoms. The experimental results agree in magnitude with theory. However, the temperature dependence determined experimentally is somewhat larger than that predicted.

There exist a number of potential explanations for the difference in the results of theory and experiment, in addition to the always possible existence of unknown systematic errors in the measurements. First, the *ad hoc* correction to the free energy of the surface atoms due to their interaction with the atoms in the vapor may be too crude an approximation. In particular, the assumption

that a surface atom sees on average the same density distribution of gas atoms, unaffected by the immediate presence of the liquid hydrogen surface, cannot be strictly correct. Second, the two-dimensional treatment of the adsorbed atoms may not be sufficiently accurate for these weakly bound systems. Vidali and Cole[16] pointed out that the motion of the adsorbed atoms perpendicular to the surface can influence the effective two-dimensional interaction among them. Third, an adsorbed helium atom may deform the liquid surface sufficiently to alter the interaction energy and the surface virial coefficient. Which, if any, of these possible reasons is correct must await more detailed calculations.

ACKNOWLEDGMENTS

APPENDIX: VIRIAL COEFFICIENTS

The values of the virial coefficients used in the analysis of the binary gas mixtures of helium and hydrogen are given in Table III. The tabulated values of the coefficients are the coefficients of the virial expansion Eq. (2), multiplied by the appropriate power of N_a, Avagadro's number, to convert to units in which the coefficients are conventionally expressed:

$$b(T) = N_a B(T), \quad c(T) = N_a^2 C(T), \quad d(T) = N_A^3 D(T) \ .$$

The virial coefficients b_{ii}, c_{iii}, and d_{iiii} for pure ^{4}He were obtained by fitting a fourth-order polynomial to the tabulated density-pressure data of McCarty,[17] with the condition that d_{iiii} is related to c_{iii} by $d = 0.581c^{3/2}$.[18] This is the relationship for the coefficients of a gas interacting via a hard-sphere potential, a good approximation for He in the temperature range of interest. The results of the fit to the data of McCarty were then smoothed and adjusted to be compatible with other measurements (see Dymond and Smith[19]).

In the case of ^{3}He there appears to be little experimental data in the temperature region of interest other than the work of Mattacotta *et al.*[20] In conjunction with that data we used the calculations of McConville and Hurley[21] for the second and third virial coefficients. The fourth virial was estimated assuming a hard-sphere potential.

The virial coefficients for pure H_2 and D_2 were taken from the work of Hord[22] and Artym, Spiridonov, and Klim,[23] respectively.

The mixed second virial coefficient b_{ij} was approximated by

$$b_{ij} = (1 - k_{ij})(b_{ii}b_{jj})^{1/2} \ , \tag{A1}$$

where k_{ij} is a parameter characteristic of the binary interaction. Hiza and Duncan[24] find a value of $k_{ij} = 0.23$ for the helium-hydrogen system, and we use that number in our analysis. In the case when b_{ii} and b_{jj} have oppo-

site signs, as is the case when ^{4}He is above 24 K and ^{3}He is above 20 K, then the model leading to Eq. (13) is not valid. Since the magnitude of b_{ij} is expected to vary smoothly with temperature, a simple extrapolation to higher temperatures was made of the low-temperature values.

The values of the mixed third virial coefficient c_{iij} were obtained following the work of Chueh and Prauznitz.[25] They use a law of corresponding states for quantum gases to determine the critical constants as a function of the virial coefficients. By relating this model to the measured dependence of the critical parameters on concentration of the two species, it is possible to estimate the mixed virials.

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