Wetting Transitions of Liquid Hydrogen Films

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Calculations are presented of the wetting properties of liquid hydrogen films on various substrates. The well depth D for the adsorption potential is even smaller for alkali metal substrates than for noble gas surfaces. A simple model calculation leads to the prediction that wetting transitions should then occur at a temperature T_w about 20 K. Quartz microbalance data obtained for H_2 on Rb are consistent with this result. Specifically, T_w is found to be 17.89 ± 0.04 K. The wetting phase diagram is found to be in good agreement with thermodynamic expectations.

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During the past year, experimental confirmation has appeared of the predictions by Cheng et al. that unusual wetting and prewetting behavior is expected for He on the alkali metals [1–6]. The fundamental origin of these phenomena is that the gas-surface interaction is extraordinarily weak. Indeed the well depth D of the adsorption potential is comparable to the characteristic energy scale of liquid He. One question which arises immediately is whether similar exotic behavior occurs in other systems. It has long been known that other noble gases do not absorb strongly on some alkali metal surfaces [7–9]; work is in progress on the theory of such systems. The present paper is devoted to the case of hydrogen adsorption. The theory described below yields qualitatively similar behavior to that obtained for the He-alkali adsorption system: Wetting transitions are expected for these surfaces in an experimentally accessible temperature range. Experimental results for H_2 on Rb are found here to be consistent with this prediction.

Carraro and Cole [10] (CC henceforth) recently obtained potentials for H_2 interacting with noble gas surfaces. Results for the well depth D and the coefficient C_3 of the asymptotic van der Waals potential

$$V \sim -C_3/z^3 \tag{1}$$

are shown in Fig. 1. The well depth values are of order 100 K, which is comparable to the ground state cohesive energy 75 K of hydrogen. The method used by CC was summation of two body potentials. This is not appropriate to the case of alkali metal surfaces due to the delocalized nature of their electrons and collective nature of the associated dielectric response. We use instead a method which has been employed for treating He adsorption on metals [11]. We write the potential as a sum of attractive and repulsive parts

$$V = V_r + V_a. \tag{2}$$

In its simplest form, the effective medium theory [12] evaluates the repulsion at distance z above the surface as a simple product of a coefficient α and the local charge $\rho(z)$ of the bare surface at the position z:

$$V_r = \alpha \rho(z). \tag{3}$$

We have adopted here the value $\alpha = 650$ eV bohrs^3 [13]. Our calculations utilize charge densities found by Lang and Kohn for the jellium model [14]. For the attraction, we have used a damped dispersion [15]:

$$V_a(z) = -\frac{C_3}{(z - z_{vdW})^3} \times \left[1 - e^{-\kappa(z - z_{vdW})} \sum_{n=0}^{2} \frac{\kappa^n (z - z_{vdW})^n}{n!} \right]. \tag{4}$$

Here the damping parameter κ has been taken from the exponential decay of the surface charge density and z_{vdW} is the reference plane position [16]. The value of C_3 has been computed from

$$C_3 = \alpha_0 E_s/8(1 + E_s/E_a), \tag{5}$$

which has been shown to work rather well for other materials [17]. In this expression, we are taking the metal to be free electronlike, with surface plasmon energy E_s. The orientationally averaged hydrogen polarizability is $\alpha_0 = 0.806$ Å^3 and its characteristic energy $E_a = 1.64 \times 10^5$ K according to Ref. [17].

Each of the various approximations has a corresponding uncertainty. Based on previous experience with He, a conservative estimate of the uncertainty in D is 40%. This is consistent with our finding that the same method applied to He yields well depths of 15.1, 14.8, 8.81, 6.91, 5.23, and 240 K for Li, Na, K, Rb, Cs, and Al, respectively, compared to corresponding values of 17.1, 10.4, 6.26, 4.99, 4.41, and 260 K obtained by more sophisticated methods [18].

Parameters characterizing our potentials are shown in Table I and Fig. 1. As with the He case, we find values of D which are even smaller than those on noble gases. The reason is the same: The electrons of alkali metal are
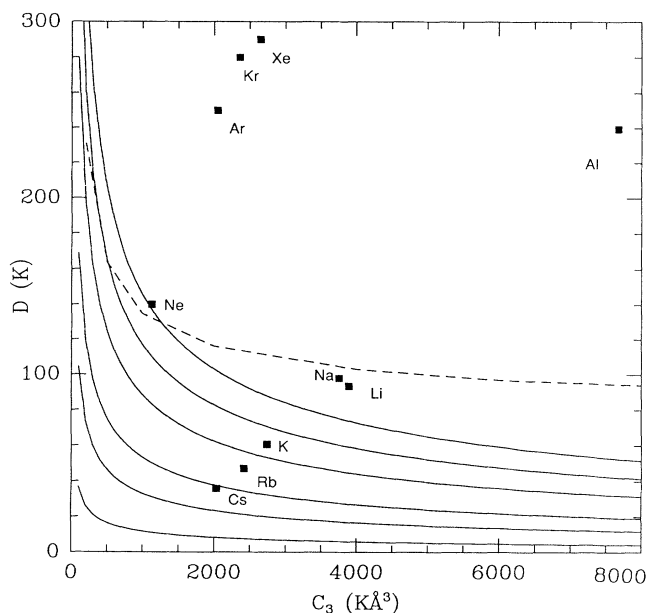
FIG. 1. The wetting phase diagram of H_2 adsorption on weak-binding substrates. The solid lines, from top to bottom, indicate the boundary separating wetting (above) and nonwetting (below) regions, with wetting temperatures $T_w = 15, 18, 21, 24, 27$, and 30 K, respectively. The dashed line, obtained variationally in Ref. [10], separates those surfaces which do not adsorb a single monolayer from those which do.

so weakly bound that they spill out quite far from the jellium edge. The resulting repulsive potential prevents the molecule from coming close to the surface, so that the van der Waals attraction is weak.

We have calculated wetting temperatures of liquid H_2 by a plausible, approximate, and surprisingly accurate method developed for the He case [1,2]. We will show elsewhere that this criterion agrees numerically with classical fluid simulation studies of Finn and Monson [19]. The energy balance which must be assessed in order to predict whether wetting will occur involves a comparison between the surface energy cost and the potential energy gain from the substrate's attraction. Wetting occurs if

$$\hat{\sigma}_{sl} + \sigma_{lv} + n \int_{z_{min}}^{\infty} dz\, V(z) \le 0 ,\qquad (6)$$

where σ_{lv} is the liquid-vapor surface tension, $\hat{\sigma}_{sl}$ is the free energy cost internal to the liquid of creating the substrate-liquid interface, z_{min} is the minimum of the po-

TABLE I. The parameters C_3 [from Eq. (5)] and D of the H_2 potential on alkali metal and Al surfaces. Also listed is the single molecule's binding energy E_b.

Substrate	Li	Na	K	Rb	Cs	Al
$C_3(K\,\text{Å}^3)$	3896	3755	2744	2420	2035	7675
D (K)	88	91	57	44	34	225
E_b (K)	55	57	32	23	16	164

tential well and n is the number density of bulk liquid H_2. We will approximate $\hat{\sigma}_{sl}(T)$ by $\sigma_{lv}(T)$. This is probably a slight underestimate of $\hat{\sigma}_{sl}(T)$ as the substrate-H_2 interface is expected to be stiffer and hence more resistant to thermal fluctuations than the liquid-vapor interface. Actual wetting temperatures may then be slightly higher than those predicted below [20]. When one evaluates the integral in Eq. (6) with a simple 3-9 model potential form [21]:

$$V(z) = 4C_3^3/27D^2 z^9 - C_3/z^3 ,\qquad (7)$$

the wetting condition becomes

$$(C_3 D^2)^{1/3} \ge 3.33\sigma(T)/n(T) .\qquad (8)$$

This equation is an equality when the temperature T is equal to the wetting transition temperature T_w. With the equality it has been used to draw the lines in Fig. 1. These "isowets" have been obtained from measured surface tension and density data, as functions of T, for bulk liquid H_2 [22]. The calculation is restricted to the domain $T > T_t = 13.80$ K, the bulk triple point, since only in this region are data for the surface tension available. We note that the predicted T_w for H_2 on Cs, K, and Rb occur well above T_t.

A modification of the energy balance has been proposed by Cole, Swift, and Toigo [23]. In this approach, one adds to the left-hand side of Eq. (6) a term ΔE_0 equal to the change in zero-point energy (ZPE) of the surface Rayleigh wave phonons when the H_2 film is added. We use the same values for H_2 as for He because ΔE_0 is actually very similar to the bare surface phonon energy of the alkali metal. The relative effect of including this term is somewhat smaller for H_2 than for He because the characteristic energy scale for H_2 is larger. Nevertheless, as seen in Table II, the effect of including ZPE is observable, i.e., a reduction by 2 to 5 K in the predicted wetting temperature. Results for deuterium are also presented in Table II. The higher transition temperatures are a consequence of its being a more classical system, as will be discussed in a more complete paper.

In Fig. 1 appears a curve calculated variationally by CC to describe the condition that the monolayer is bound more strongly than bulk hydrogen at zero temperature. Not surprisingly, this microscopic result is qualitatively similar to the wetting curves obtained here. The same situation prevails for He [10].

TABLE II. The wetting temperature T_w of H_2 on substrates Cs, Rb, and K, calculated without a phonon zero-point energy correction (Fig. 1) and its values with the correction included on (110) and (100) facets [23]. Values in parentheses are for D_2.

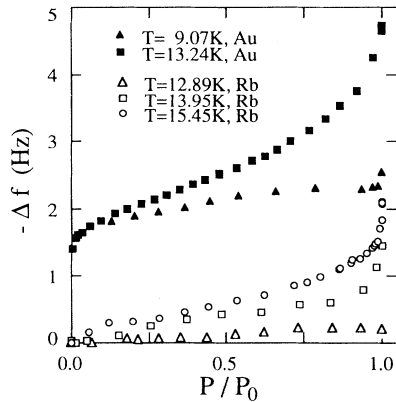| Substrate	T_w (K)	$T_w^{(100)}$ (K)	$T_w^{(110)}$ (K)
Cs	24(32)	22(30)	21(29)
Rb	22(30)	20(28)	18(26)
K	20(28)	17(25)	15(23)

FIG. 2. Adsorption isotherms on bare gold and on rubidium evaporated onto gold. The frequency values have been corrected for pressure effects. One Hz corresponds to a 5.6 Å film of H_2. The increase in H_2 adsorption on Au as the temperature is moved toward the H_2 triple point is a well known manifestation of triple point wetting.

Anticipated to accompany the first-order wetting transitions predicted here are prewetting (thin film to thick film) transitions. These transitions, which are the natural extensions of first-order wetting transitions away from liquid-gas coexistence, will terminate in critical points, as observed for the case of ^{4}He on Cs [1,2,6]. If the variational result of CC is correct, for example, one can say that systems with values of D and C_3 lying below the dashed line in Fig. 1 exhibit, at low T, either nonwetting or wetting at coexistence with, in the latter case, accompanying prewetting transitions off coexistence.

These predictions have been borne out in data we have obtained for H_2 on Rb. The experiments use a quartz microbalance in which the mass of the adsorbed film is detected by a drop in the resonant frequency of the quartz crystal. We used a commercial, but individually selected, AT-cut quartz crystal with gold plated electrodes excited at the fifth harmonic at 16.7 MHz [24]. The crystal is mounted horizontally inside the cell, each electrode facing a Rb dispenser [25]. A shutter controlled by a stepping motor is placed between the two dispensers and the crystal. During the evaporation in vacuum, the wall of the sample cell is maintained at liquid nitrogen temperature and a current is passed through the filaments. When the current reaches the filament characteristic emission value, the shutter is quickly opened and the two gold electrodes are exposed to the Rb for about one minute. The shutter is then closed, the current turned down to zero, and the cell cooled to helium temperature right away. From the drop in frequency after the evaporation we estimate that the Rb film is about 500 Å thick. To measure the quartz resonant frequency we adopted the ferromagnetic modulation technique first used by Lea, Fozooni, and Retz [26]. The frequency resolution is about 0.05 Hz for an excitation power of less than 20 nW.
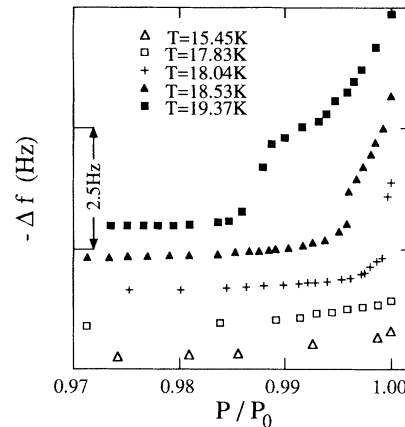
Figure 2 shows the resulting frequency shift for various

FIG. 3. Adsorption isotherms on Rb taken below and above the wetting temperature $T_w = 17.89$ K. The isotherms have been vertically shifted for greater clarity.

values of T near the H_2 triple point T_t on bare gold and on gold evaporated with rubidium. It clearly displays the spectacular difference between the two substrates: On Rb there is virtually no adsorption at low pressures, while on gold an H_2 film about 7 Å thick is present even at $P/P_0 = 0.05$. On Rb below the H_2 triple point, T_t, there is almost no adsorption even at $P = P_0$. At 15.45 K the adsorbed H_2 film is about 12 Å thick at $P = P_0$, indicating incomplete wetting.

Figure 3 displays four isotherms taken near 18 K on a very expanded scale close to $P = P_0$. For comparison, the isotherm at 15.45 K is also shown. There is a qualitative difference between the isotherm taken at 17.83 K and those at higher temperatures. The isotherm at 17.83 K shows incomplete wetting at coexistence similar to that found at 15.45 K. In contrast, the isotherm at 18.04 K displays a discontinuous increase in coverage very close to $P = P_0$. As T is increased, the location of this rise moves to lower relative pressures: at $T = 19.37$ K, it is found at $P/P_0 = 0.987$. We identify this discontinuity as the prewetting or thin film to thick film transition. These results are suggestive of a wetting temperature T_w between 17.83 and 18.04 K. The limiting adsorbed film thickness of the 18.04 K isotherm is found to be smaller than that at higher temperatures. We believe this result, as well as the rounding found at the prewetting jumps in the 18.53 and 19.37 K isotherms, is related to the limited temperature stability of our sample cell. In our experiment, the temperature of the sample cell was regulated to ± 2 mK, which translates to a stability in the relative pressure of about 1.5×10^{-3}. The imperfections of the Rb surface may also contribute to the observed rounding.

Figure 4 displays the location of the prewetting jumps, expressed in terms of chemical potential difference relative to the saturation value, at various temperatures. We identify the position of each prewetting jump, P_{step}/P_0, as that corresponding to the maximum slope of the isotherm. The solid line in Fig. 4 represents a nonlinear least
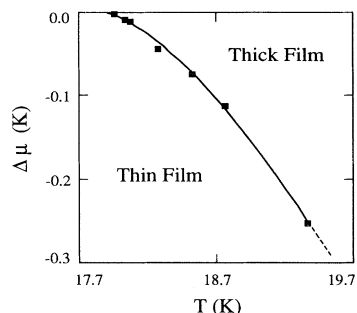
FIG. 4. Phase diagram of the prewetting transition. $\Delta\mu(T)$ is the chemical potential difference (relative to the saturation value) of the transition at temperature T. The solid curve is discussed in the text.

squares fit of the data to the form

$$-\Delta\mu = \mu_{\text{sat}}(T) - \mu_{pw}(T) = a(T - T_w)^\beta, \qquad (9)$$

where $\Delta\mu = kT \ln(P_{\text{step}}/P_0)$, and a, T_w, and β are parameters of the fit. The best values for the parameters, with corresponding uncertainties (equal to the one-sigma values) are $T_w = 17.89 \pm 0.04$ K, remarkably close to the predicted value (18–20 K); $\beta = 1.47 \pm 0.08$, in good agreement with the value of $\frac{3}{2}$ deduced from thermodynamic arguments [27]; and $a = 0.14 \pm 0.01$ K$^{1-\beta}$. (The uncertainties quoted above do not include possible systematic errors.) The value of a derived from theoretical predictions is

$$a = \left[\frac{2}{3} \frac{\partial\sigma}{\partial T} \frac{1}{\rho\Delta C_3^{1/3}} \right]^{3/2} \simeq 0.23 \text{ K}^{-1/2}. \qquad (10)$$

In conclusion, we have calculated adsorption potentials for H_2 on alkali metal surfaces. The results, as for He, are very shallow well depths. Using a simple criterion to characterize the transition, we predict wetting to occur in the liquid regime of the phase diagram for most alkalis. The first data testing thus has been presented; the wetting temperature for H_2/Rb was found to agree remarkably well with the theory. Remaining to be done are both a more realistic treatment of the statistical mechanics and experimental tests for other H_2 and D_2 adsorption systems [28].

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