

## Triple-point wetting of H<sub>2</sub> films adsorbed on silver

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The wetting behavior of H<sub>2</sub> films adsorbed on silver was studied with a quartz-crystal microbalance. Below the triple-point temperature  $T_t$ , incomplete-wetting films are observed, while above it the liquid films completely wet the substrate. Within the experimental resolution the wetting transition occurs at  $T_t$ . The maximum frequency change at saturation (which corresponds to the film thickness at saturation) increases as the temperature approaches  $T_t$ , obeying a power law of the form  $\Delta f_0 \alpha t^{-1/n}$ , with  $n = 3.28 \pm 0.3$  and  $t = (T_t - T)/T_t$ . The shape of the isotherms suggests the presence of two-phase films above and below the triple point.

### INTRODUCTION

The study of the growth modes and wetting of physisorbed films is attracting considerable theoretical<sup>1-4</sup> and experimental<sup>5-20</sup> attention. Multilayer films can grow in one of two ways on an attractive substrate: Either the thickness of the film increases with increasing pressure, diverging as the saturated vapor pressure is approached (complete wetting), or the thickness of the film remains finite and at saturation bulk coexists with a finite-thickness film (incomplete wetting).

For a given adsorbate-substrate combination a transition may occur from incomplete to complete wetting as a function of temperature.<sup>1</sup> The most frequent type of wetting transition observed is "triple-point wetting."<sup>9</sup> In its simplest form, triple-point wetting is a transition which evolves continuously from an incomplete-wetting solid film at low temperature to a complete-wetting liquid film at a wetting temperature  $T_w$  at or near the triple point  $T_t$ . Structural mismatch between the film and the substrate is responsible for the finite thickness of the solid film.<sup>3,4</sup> More complicated situations are also possible near a triple point.<sup>2</sup> Alternatively, there also exist systems which can form very thick films on both sides of the triple point (namely Ar, Kr, and Xe on graphite<sup>18</sup>), which are interpreted as complete wetting.

Multilayer H<sub>2</sub> films have been studied on a graphite substrate only by volumetric adsorption isotherms<sup>6</sup> and with a graphite-fiber microbalance.<sup>13</sup> The volumetric study measured isotherms above and below the triple point. It found no evidence of incomplete-wetting behavior throughout the whole temperature interval. It should be noted, however, that the films were studied only up to thicknesses of approximately six layers.<sup>6</sup> The graphite-fiber microbalance studied only films above the triple point, where thick films could be formed.<sup>13</sup>

The wetting behavior of quantum films, particularly that of <sup>4</sup>He, is presently a matter of very active research and controversy.<sup>12,13,20-22</sup> H<sub>2</sub> films, which due to their light molecular mass are also quantum, offer another system in which to study what relationship (if any) exists between the quantum nature of a system and its wetting properties.

### EXPERIMENTAL

We measured a series of vapor-pressure adsorption isotherms using a quartz-crystal microbalance. Our experimental setup consists of two 8-MHz, AT-cut, silver-plated, commercially available quartz crystals. One of them, the balance crystal, is exposed to the H<sub>2</sub> gas. The other crystal, the reference, is maintained inside an evacuated, sealed container contiguous to the balance crystal and at the same temperature. During the course of an isotherm the change in the difference between the frequencies of the balance and reference crystals ( $\Delta f$ ) is monitored as a function of the pressure inside the sample chamber. For an adsorbed solid film  $\Delta f$  is directly proportional to the mass of H<sub>2</sub> adsorbed on the balance crystal. Direct proportionality between  $\Delta f$  and the mass adsorbed also holds for liquid films, provided that the thickness of the liquid film is smaller than one-half the viscous penetration length. Throughout the experiments reported here this condition was satisfied.

The experimental apparatus is similar to that described in previous work from this laboratory<sup>9,10</sup> with the important modification that the reference crystal (which in previous experiments had been placed outside the sample chamber, at room temperature) was placed inside the experimental chamber. This was done in order to improve the stability of the frequency difference during the experiment. One layer of H<sub>2</sub> on the quartz crystal results in  $\Delta f \approx 0.8$  Hz. With the modification we were able to achieve a stability in the frequency difference of the order of  $\pm 0.05$  Hz, less than one tenth of a layer of H<sub>2</sub>.

The pressures were measured using MKS capacitance gauges. The isotherms were measured introducing the H<sub>2</sub> gas in small increments into the experimental cell. The values for the temperatures in this experiment were determined from the measured values of the saturated vapor pressures of H<sub>2</sub> by using the most recently published pressure-temperature coefficients available in the literature.<sup>23</sup> For temperatures below the triple point the determination of temperatures from the saturated vapor pressures is accurate to within  $\pm 10$  mK. Near the triple point a difference in temperature of 10 mK corresponds to a difference in saturated vapor pressure of 0.34 Torr.

Our temperature resolution is on the order of  $\pm 1$  mK. Since, in our experimental setup, we have no independent way of determining the triple point, our determination of it is limited by the accuracy of our temperature scale. The limitations in the determination of the value of  $T_w$  and that of the growth mode exponent for this system introduced by the uncertainties in the temperature scale will be discussed below.

## RESULTS

We measured 11 isotherms below the triple point. They ranged in temperature from 1.486 to 0.003 K below it. We also measured four isotherms above the triple point; they ranged in temperature from 0.017 to 0.660 K above it. The triple-point coordinates are  $T_t = 13.956$  K and  $P_t = 54.00$  Torr.<sup>23</sup>

### Behavior below the triple point

Figure 1 presents a representative sample of isotherms taken below  $T_t$ . Two important features are readily apparent in these isotherms. First,  $\Delta f_0$ , the net change in frequency at the saturated vapor pressure  $P_0$  is finite. This is a clear indication that the thickness of the adsorbed films is finite at  $P_0$ , i.e., that the film incompletely wets the substrate. Second, the value of  $\Delta f_0$  increases as  $T \rightarrow T_t^-$ . These two features are characteristic of systems exhibiting triple-point wetting.<sup>9-11</sup>

A useful way of presenting isotherm data is suggested by the Frenkel-Halsey-Hill (FHH) model of adsorption.<sup>24</sup> This model describes isotherms for a complete-wetting film when the interaction between adsorbate and substrate is described by  $u(z) = -az^{-3}$ . The FHH isotherm equation is

$$k_B T \ln(P_0/P) = \alpha d^{-3}, \quad (1)$$

where  $d$  is the thickness of the adsorbed film, and  $\alpha$  is the effective interaction parameter. In Fig. 2, we show the isotherm for  $T = 13.930$  K (0.026 K below  $T_t$ ) plotted in terms of  $\log_{10}(P_0/P)$  versus  $(\Delta f)^{-3}$ . With this choice of axes a complete-wetting isotherm would pass through the origin. The finite intercept at saturation in Fig. 2 indicates a limiting thickness of about 23 layers. The deviation from linearity in Fig. 2 is similar to the behavior which has recently been reported for neon films using the same technique,<sup>10</sup> and will be discussed later.

It has been observed before that for systems exhibiting triple-point wetting the maximum thickness of the adsorbed film at saturation increases as the temperature approaches the triple-point temperature.<sup>9-11</sup> A simple phenomenological model proposed by Krim *et al.*<sup>9</sup> predicts

$$d_0 = At^{-1/n}, \quad (2)$$

with  $d_0$  the maximum film thickness at saturation,  $t = (T_w - T)/T_w$ , and  $n = 3$ . The value of  $n$  originates from the range dependence of the adsorbate-substrate potential.<sup>9</sup>

In Fig. 3 we present a logarithmic plot of  $\Delta f_0$  versus the reduced temperature  $t$ , with  $t = (T_t - T)/T_t$ . The be-

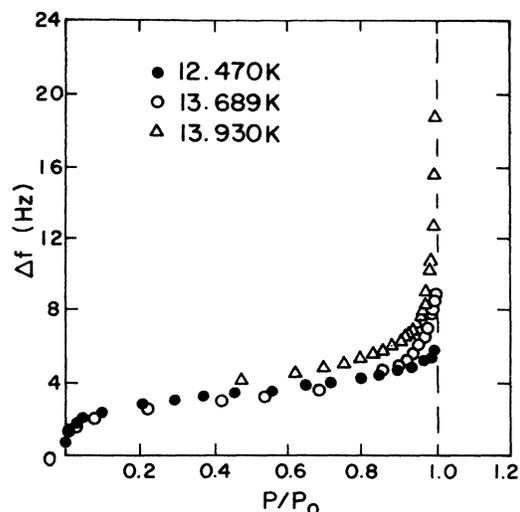


FIG. 1. Frequency change vs  $P/P_0$  isotherms for three temperatures below  $T_t$ : ● = 12.470 K, ○ = 13.689 K, △ = 13.930 K.

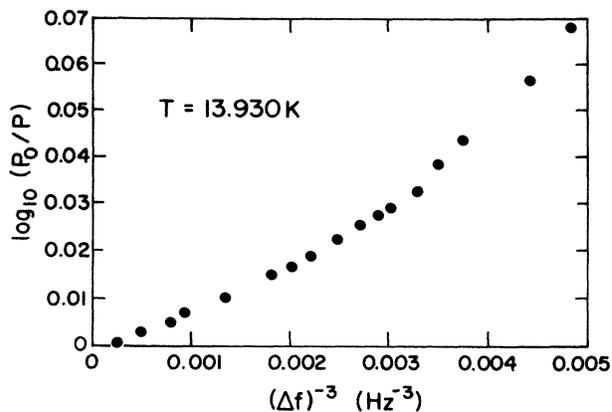


FIG. 2. Isotherm taken at 13.930 K, 0.026 K below  $T_t$ . The coordinate axes are suggested by the FHH equation. The film thickness at saturation corresponds to 23 layers.

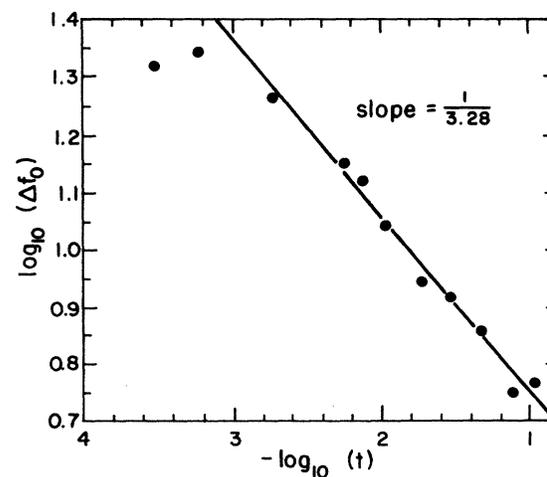


FIG. 3. Logarithmic plot of the frequency change at saturation vs  $t$ , with  $t = (T_t - T)/T_t$ . The rounding observed for small  $t$  is discussed in the text.

havior follows the form of Eq. (2) with  $n = 3.28 \pm 0.3$ . The large uncertainty in  $n$  due to the 10 mK uncertainty in our determination of  $T_i$ .

Within the resolution of our experiment the wetting temperature for this system coincides with the bulk triple point  $T_w = T_i \pm 0.010$  K. With the exception of the two isotherms measured closest to  $T_i$  (respectively, 0.08 and 0.003 K below it), all others clearly show a finite intercept at saturation (see Fig. 2). The measured values of  $\Delta f_0$  for the two isotherms closest to  $T_i$  correspond to thicknesses of 28 and 26 layers. The temperatures at which these isotherms were measured fall within the estimated uncertainty of our determination of  $T_i$ .

For temperatures close to the triple point, Fig. 3 shows significant rounding. This behavior is to be expected, as the films become increasingly thick. The value of  $n = 3$  in Eq. (2) is obtained assuming that the films are sufficiently thin so that retardation effects in the potential can be neglected.<sup>25</sup> For thicker films, terms of order higher than  $z^{-3}$  have to be included. This will result in values of  $n$  larger than 3. Another important effect is the thinning of the films caused by the presence of thermal gradients, with the microbalance crystal at a temperature  $\Delta T$  higher than the coldest point inside the sample cell. This effect has recently been discussed by Taborek.<sup>12,13</sup> Even a complete-wetting film has only finite thickness at saturation in the presence of a thermal gradient. Using parameters corresponding to  $H_2$  a temperature difference of  $\Delta T = 0.0006$  K will result in a maximum film thickness at saturation of 35 layers for temperature above  $T_i$ . This limit in the thickness of the films is more apparent for temperatures closer to  $T_i$ , where the films should be thicker. This can produce the rounding in the data observed in Fig. 3. The presence of a gravitational potential difference between the microbalance and the bottom of the sample cell will also result in a thinning of the film; however, this effect is much smaller (by at least a factor of 5) than that due to thermal gradients.

#### Behavior above the triple point

The four isotherms measured above  $T_i$  are consistent with complete wetting, with maximum thickness at saturation limited by the possible presence of a thermal gradient in the cell of the order of 0.0006 K. Figure 4 presents the results for  $T = 14.616$  K. The maximum frequency change measured at saturation corresponds to a thickness of 36 layers. The average maximum thickness measured for the four isotherms above  $T_i$  was 35 layers. In Fig. 4 an isotherm obeying the FHH equation [Eq. (1)] would be a straight line. The isotherm, however, deviates from linearity, and so do the other three isotherms measured above  $T_i$ . As noted above, this behavior had been seen before for Ne isotherms.<sup>10</sup> In that case, it was explained using a two-phase slab model in which the films above  $T_i$  are assumed to be composed of two phases;<sup>26</sup> a solid slab near the substrate, with the solidification induced by the attractive substrate in equilibrium with a thicker liquid film above it. The model has been described in detail before.<sup>10,26</sup> The thickness of the solid slab is given by

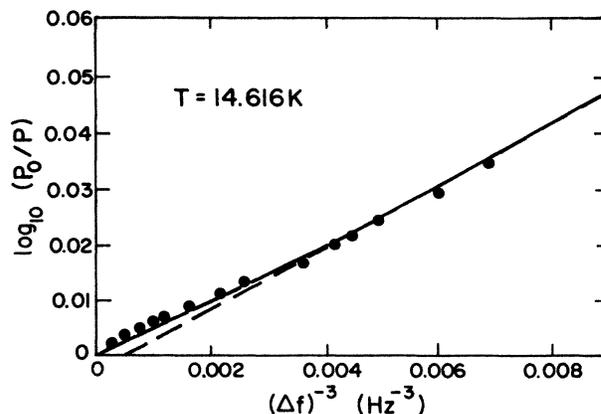


FIG. 4. Isotherm taken above the triple point at  $T = 14.616$  K. Points represent the experimental data. The continuous curve is the result of a single parameter fit to the two-phase slab model. The dashed curve is a straight line, plotted for reference. The deviation between the data and the slab model can be attributed to appreciable compression of the solid phase; whereas the model assumes constant density of each phase. A compression ranging from 7% to 19% above the solid density at the melting pressure would bring the calculated curve into agreement with the data.

$$d_s = (\{1 - \exp[-K_l(P_m - P_0)]\} / K_l \rho_l \alpha + d^{-3})^{-1/3}, \quad (3)$$

where  $K_l$  is the liquid compressibility,  $P_m$  the melting pressure,  $P_0$  the saturated vapor pressure,  $\rho_l$  the average liquid density, and  $d$  the total film thickness. The value for the total thickness  $d$  is obtained using Eq. (1). The frequency response of the quartz-crystal microbalance is given by

$$\Delta f = \gamma[\rho_l d + (\rho_s - \rho_l)d_s], \quad (4)$$

where  $\gamma$  is the mass sensitivity of the crystal.

All isotherms above  $T_i$  were fitted using this model, in which the sensitivity of the crystal was left as the only free parameter, and published values for  $H_2$  were used for  $P_m$ ,  $P_0$ ,  $K_l$ ,  $\alpha$ ,  $\rho_l$ , and  $\rho_s$ .

For the microbalance the expected mass sensitivity can be calculated from resonant frequency, elastic constants, and density of quartz. In our case the expected sensitivity of the crystal is 9.6 (Hz  $\text{\AA}^2$ )/molecule of  $H_2$ , using room temperature values for the quartz parameters. The fitted values of  $\gamma$  ranged from  $\gamma = 9.97$  (Hz  $\text{\AA}^2$ )/molecule of  $H_2$  (for the 14.150 K isotherm) to  $\gamma = 12.59$  (Hz  $\text{\AA}^2$ )/molecule of  $H_2$  (for the 13.973 K isotherm). This difference with respect to the theoretical value is not unreasonable, since the measurements were performed at low temperatures. A similar behavior was observed in the neon experiment.<sup>10</sup>

The solid curve in Fig. 4 is a result of the described fit. The fits to the data are reasonable, but the agreement between the data and the model is not as good as it was in the neon case.<sup>10</sup> The two-phase slab model assumes that the densities in the solid and liquid phases are constant

throughout each phase and that the compressibility is independent of pressure. These assumptions are followed more closely by neon than by H<sub>2</sub>.

### CONCLUSIONS

Our measurements show that H<sub>2</sub> films adsorbed on silver exhibit triple-point wetting, a behavior similar to that which is shown by a series of other, purely classical films. The results below the bulk triple point are different from those reported for H<sub>2</sub> films on graphite.<sup>6</sup> While different wetting behavior on different substrates is to be expected and has been observed on graphite<sup>18</sup> and on gold<sup>9</sup> for Ar, Kr, and Xe, it should be pointed out that the smallest film thickness at saturation measured in our

experiment was of seven layers at the lowest temperature measured, while the experiments on graphite extended only to a maximum thickness of about six layers.<sup>6</sup> Above the triple point quite thick films could be formed, the same kind of behavior observed on previous experiments on graphite.<sup>13</sup> The thicknesses at  $T > T_i$  appeared to be limited only by the presence of thermal gradients of order 0.0006 K inside the sample cell. The shape of isotherms both above and below the triple point suggest the presence of stratified two-phase films.

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