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Wetting phenomena in films of molecular hydrogen isotopes

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We have investigated various aspects of the wetting behavior of hydrogen films (including the heavier isotopes) using surface plasmon resonance, light scattering, and photoelectron emission. Studies in the vicinity of the triple point ($T_3(H_2) = 13{,}96$ K) confirmed the known «triple point wetting», and gave no indications for a prewetting transition in this range. At low temperatures ($T < T_3/3$) the equilibrium film thickness reaches only a few monolayers. Thicker films, prepared by quench-condensation of H_2 gas at 1.5 K, undergo a dewetting process during annealing: most of the film material contracts to clusters, and in between the films thins down to its equilibrium thickness. This surface diffusion process is thermally activated, with an activation energy of 23 K (in the case of H_2). The dewetting kinetics has not revealed any indication for a surface-molten layer on the solid films at low temperatures, or for a superfluid component.

1. Introduction

The adsorption of weakly bound (physisorbed) films is a topic of long-standing interest, motivated also by the relevance of such films for many applications. Nevertheless, important details of the underlying processes which govern the behavior of physisorbed films have been discovered only recently. In this context the quantum systems of helium and hydrogen have played an important role as particularly clean and, regarding their basic interactions, relatively simple systems. Among the most striking phenomena were the «nonwetting» of Cs substrates by ^{4}He at sufficiently low temperatures, and the discovery of a prewetting transition in the same system [1,2]. For molecular hydrogen, so-called triple-point wetting has been found, i.e. complete wetting above and incomplete wetting below the triple point temperature T_3 [3,4].

Particular interest in hydrogen films stems from the fact that the topmost layers appear to remain liquid down to temperatures far below T_3 [5], and one might speculate that, due to zero-point motion, this state could extend even down to zero Kelvin. If so, such a surface-molten layer should become superfluid at sufficiently low temperatures.

We describe here investigations of physisorbed films of molecular hydrogen (including also the heavier hydrogen isotopes, although for our examples we have mainly chosen H_2), both in equilibrium and nonequilibrium, metastable states. For the latter case the films, when carefully annealed, undergo partial dewetting [6]. It turns out that wetting phenomena in these films are not only interesting in themselves, but are also crucial for the interpretation of experiments which at first sight might appear as not being related to the topic of wetting.

2. Experimental

Most of the data on hydrogen films presented here were obtained using the surface plasmon resonance technique (also called ATR = attenuated total reflection method), which provides very accurate information both about the thickness and the roughness of the physisorbed material. Details of this method are described in Ref. 7. The surface plasmons (SP) propagate in a thin metal film (in our case Au or Ag) on a glass prism and are excited by a laser beam impinging at a certain resonance angle θ_R. The plasmon generation manifests itself in a sharp drop of the reflected light intensity at that particular angle. Adsorbing a dielectric film onto the metal surface leads to a shift of the resonance towards larger angles. For films with a thickness d, small compared to the decay length of the evanescent field of the SP (which is on the order of the wavelength of light), this shift is proportional to d and therefore can serve to determine the film thickness. Moreover, information about a possible roughness of the adsorbed film is gained from the increase in the resonance width, and from the intensity of scattered light resulting from the decay of SP mediated by the interaction with surface irregularities.

As a second method, we introduce here the photoemission of electrons through a physisorbed hydrogen film. Starting again with a clean silver surface, we

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measure the current due to photoelectrons excited when the film is illuminated with UV light. (The energy of the light quanta here was $h\nu \approx 4$ eV, slightly above the work function of our silver film, $W \approx \approx 3.5$ eV.) If the metal is now covered with a continuous H_2 film of homogeneous thickness, the photocurrent will drop quickly because the kinetic energy of the emitted electrons is not sufficient to overcome the energy barrier that the surface of condensed hydrogen provides against electrons to enter the bulk phase, roughly 3 eV [8]. The only way for the electrons to penetrate the hydrogen film is therefore to tunnel through this energy barrier, which gives rise to an exponential decrease of the photocurrent as the film thickness d is increased. If the film material is distributed inhomogeneously, with areas thinner than the mean coverage, tunneling will preferentially take place at those thin regions, and the photocurrent will increase compared to the homogeneous case. In this way an additional clue for the dewetting process of quench-condensed films was obtained, as shown below in Sec. 4.

3. Films in equilibrium

In order to demonstrate the efficiency of the SP technique we give in Fig. 1 an example of the formation of a H_2 film on gold as a function of the gas pressure in the sample cell. The temperature was 9.93 K, 4 K below the triple point temperature $T_3(H_2) = = 13.9$ K. The adsorption isotherm displays clear steps, which show a layer-wise growth of the hydrogen film and simultaneously indicate that the gold substrate was sufficiently smooth to allow the formation of well-defined monolayers. At higher temperatures the step structure is less pronounced due to thermal broadening, as seen in Fig. 2.

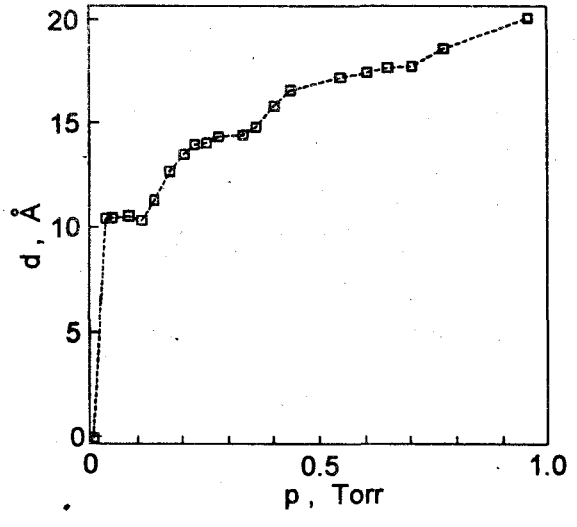

Fig. 1. Film thickness vs. gas pressure of H_2 on gold at temperature $T = 9.93$ K. Only the low pressure part of the adsorption isotherm between $p = 0$ and 1 Torr is shown (saturated vapor pressure $p_s = = 1.8$ Torr at this temperature). The plateaus correspond to the third, fourth and fifth monolayer (the first two layers are already completed at very low pressure and were not resolved here).

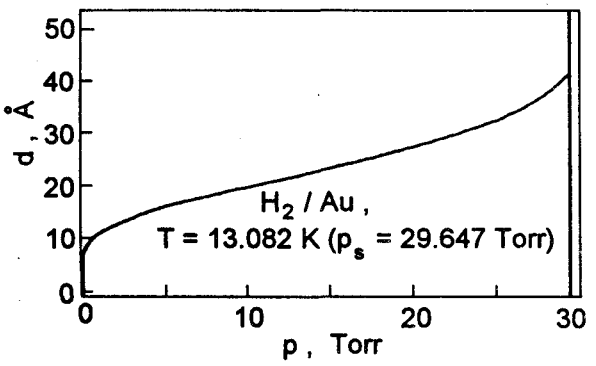

Fig. 2. Adsorption isotherm of H_2 on gold at $T = 13.082$ K (after Ref. 4).

Figure 2 shows also another feature, relevant at high gas pressures close to the saturated vapor pressure p_s: although the film thickness increases continuously with p in this range, it apparently approaches a finite value d_s for $p \to p_s$. This behavior qualitatively holds for all temperatures $T < T_3$, in contrast to the temperature range $T > T_3$, where the film thickness appears to diverge for $p \to p_s$. As already mentioned before, this is the triple point wetting phenomenon known for hydrogen as well as for several other simple systems [3,4,9]. It is illustrated in its temperature dependence in Fig. 3. In this measurement the sample cell contained a small amount of bulk hydrogen at the cell bottom, so that the gas pressure was always close to p_s, and hence the film thickness close to d_s *. The rapid variation of the film thickness just below T_3 is obvious. The dependence closely follows a power law, $d_s \propto (1 - T/T_3)^{-\alpha}$, with $\alpha = 1/3$ (Fig. 4). This is exactly the behavior expected for systems with van der Waals interaction, and has been found similarly also for other adsorbate-substrate combinations [9].

* Due to the finite height of the probed surface above the bulk H_2 material and a small temperature gradient in the sample cell the film thickness had a value slightly less than at liquid-vapor coexistence; for film thicknesses below 100 Å, however, this effect was estimated to be negligible.

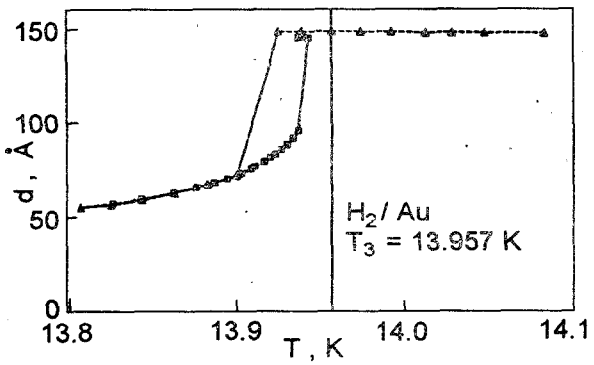

Fig. 3. Film thickness d_s of H_2 on gold at saturated vapor pressure vs. temperature. The triangles were taken on cooling, the squares on heating (after Ref. 4).

In the immediate vicinity of T_3 some hysteresis is observed, which depends on the details of the experimental procedure, and appears to be related to the supercooling of the liquid phase when one reduces the temperature, starting from above the triple point. We have also checked the suggestion that the observed hysteresis might be related to a prewetting transition [2]. For that purpose a series of adsorption isotherms was taken in the temperature range around T_3. Prewetting would manifest itself in an additional structure in the otherwise smooth S-shaped adsorption curve like in Fig. 2. The data show no indication of such an anomaly, we have therefore no hint that a prewetting transition occurs for H_2 on gold in the heighborhood of the triple point.

An extrapolation of the temperature-dependent saturated film thickness in Fig. 4 to temperatures well below T_3 (say, $T \leq T_3/3$) yields a limiting value of d_s of about 15 Å. Although an extrapolation over such large a temperature interval cannot be expected to

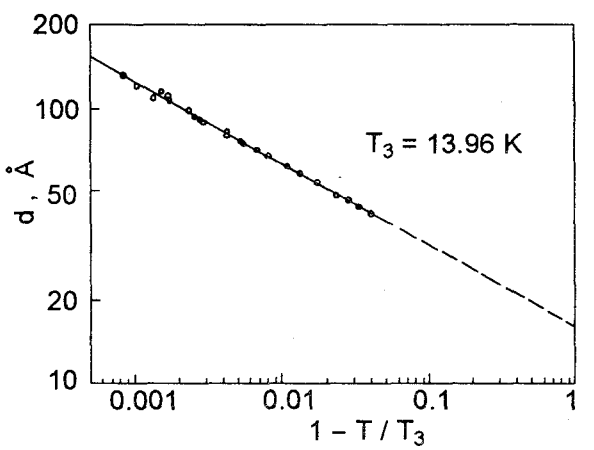

Fig. 4. Logarithmic plot of the film thickness d_s below T_3 (data of Fig. 3) vs. the reduced temperature difference. The slope of the straight line is 1/3.

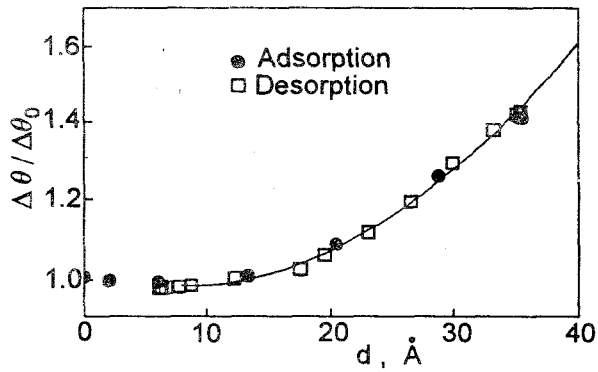

Fig. 5. Reduced SP resonance width $\Delta\theta/\Delta\theta_0$ vs. film thickness for D_2 on silver. The adsorption data were taken at $T = 4.2$ K, desorption data at 4.6 K. The duration of the adsorption and desorption process was 30 min in each case.

yield correct numbers, the estimate obtained in this way appears to be realistic. We infer this from results of an experiment with a quasi-equilibrium film around 5 K, shown in Fig. 5, where the molecules (D_2 in this case) were condensed from a gas stream supplied through a capillary from the outside. The background gas pressure in this cell was kept well below 10^{-6} Torr by means of cryopumping. The adsorbed film was therefore controlled in its thickness by the dynamic equilibrium between molecules condensing on the surface from the gas stream and those desorbing and being pumped away. Plotted in Fig. 5 is the reduced width of the SP resonance, $\Delta\theta/\Delta\theta_0$ (where $\Delta\theta_0$ is the width without adsorbate), which is a measure of the film roughness, vs. the film thickness as obtained from the SP resonance angle. Apparently the film is smooth (i.e. the reduced width is $\Delta\theta/\Delta\theta_0 = 1$) up to a thickness around 12 Å. Beyond that value the SP resonance width starts to broaden considerably. We interpret this dependence as the build-up of a smooth, homogeneous film up to a limiting thickness d_1 of 3 to 4 monolayers, beyond which the condensing molecules aggregate to from bulk crystallites. Such a behavior is known from usual film deposition as «Stranski-Krastanov growth». In terms of wetting scenarios this corresponds to incomplete wetting, with d_1 being equivalent to the maximum thickness d_s introduced above. Indeed, the value of d_1 derived from Fig. 5 is in satisfactory agreement with the extrapolated value of d_s in Fig. 4. That the structure of the film is close to its equilibrium configuration in this experiment — irrelevant of the way how the film was prepared — is seen from a comparison of the data taken during growth and desorption. The two data sets yield essentially the same $\Delta\theta$ vs. d dependence, hence nonequilibrium or hysteresis effects can only play a minor role.

As a consequence, these experiments show that at low temperature homogeneous hydrogen films in equilibrium can be grown on «usual» substrates like Ag or Au only to a thickness of a few monolayers. If a thicker film, prepared at higher T, is slowly cooled, its thickness will decrease, with the surplus material either desorbing or coagulating on the film to form bulk crystallites (depending on the experimental conditions). This effect, which is a general film phenomenon, has in particular to be taken into account in experiments with the hydrogens, because, as shown in the next section, this coagulation process can take place there at surprisingly low temperatures.

4. Metastable quench-condensed films

The data displayed in Fig. 5 imply that in this experiment the mobility of the adsorbed molecules at the surface was sufficiently large to allow the agglomeration process to occur on a time scale short compared to the adsorption or desorption cycle, which was 1/2 hour. If this high mobility were caused by a surface-molten layer, which might survive, as pointed out in the introduction, even down to $T = 0$, a behavior similar to the one in Fig. 5 should be observed also at distinctly lower temperatures. In order to study this question we have repeated the experiment with the substrate now being cooled to 1.5 K during the film deposition process. At that temperature the vapor pressure of hydrogen is well below 10^{-12} Torr, so desorption should be negligible here. Thus all the molecules once adsorbed should remain in the film during the measurement. Figure 6 confirms this expectation. It shows the growth of a film, prepared by condensing H_2 gas from the feeding capillary for 2 minutes. Then the gas flow was stopped, and the film thickness saturated and was stable at a value of 52 Å.

The simultaneous registration of the resonance width (not shown here) revealed that $\Delta\theta$ was not affected by the H_2 condensation, quite in contrast to the film in Fig. 5, and in spite of the fact that here the film was grown even to a considerably larger thickness. This means that at the preparation temperature $T = 1.5$ K the film was smooth and homogeneous on an optical length scale; coagulation as in Fig. 5 did not occur. Diffusion in the film must therefore have been strongly suppressed as compared to 5 K. We take this as a clear signature that a surface-molten layer does not exist on solid H_2 at 1.5 K.

Since the molecular mobility is so small that diffusion cannot take place, a film quench-condensed at such a low temperature is expected to be strongly disordered. Yet the film inhomogeneities will not show up as a broadening of the SP resonance as long as their typical size is on an atomic scale, much smaller than the plasmon wavelength. If one then raises

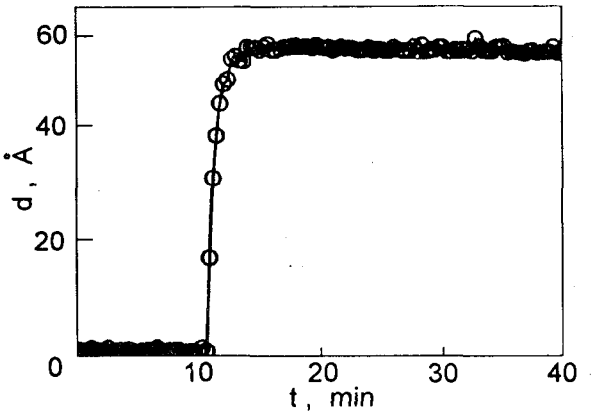

Fig. 6. Growth of a quench-condensed H_2 film on a silver substrate at $T = 1.5$ K. The temperature of the gas molecules was roughly 20 K. The valve to the external gas supply was opened at $t = 10$ min and closed two minutes later.

the film temperature, so that surface diffusion processes set in, the film will start to relax in its structure, and crystallites on a homogeneous thin equilibrium film will develop. Once this occurs the SP resonance width should start to increase.

The result of such an annealing experiment, where the film temperature was slowly increased at a rate of 1 K/h, is presented in Fig. 7. The initial film thickness was 125 Å. In addition to the SP signals we have also plotted in Fig. 7 the intensity of light scattered by the H_2 film in the area where the surface plasmons were excited, which yields additional information about the film roughness. All three signals are essentially constant up to a temperature of about 2.8 K, and show no indication of annealing effects in this range. Above that temperature, there is a strong increase in SP width (Fig. 7,*b*) as well as in the scattered light intensity (Fig. 7,*c*), accompanied by a similarly drastic change in the SP resonance angle (Fig. 7,*a*). Above 3 K the signals again remain approximately constant, until eventually desorption sets in around 3.6 K.

These observations are readily interpreted in terms of the above-mentioned coagulation or dewetting model. Apparently at a temperature of 2.8 K the diffusion processes are fast enough for the film to relax towards its quasi-equilibrium dewetted state within a few minutes. From the anisotropy of the light scattering (Fig. 7,*c*) one can conclude that the scattering centres, which we identify with the crystallites on top of the homogeneous film, must have a size comparable to or even larger than the light wavelength. Additional evidence for crystallites on this length scale is provided by measurements with surface acoustic waves by Weiss and coworkers [10]. The apparent drop in the film thickness in Fig. 7,*a* then follows from the fact that the crystallites are so large that their tops are not within reach of the evanescent field of the plas-

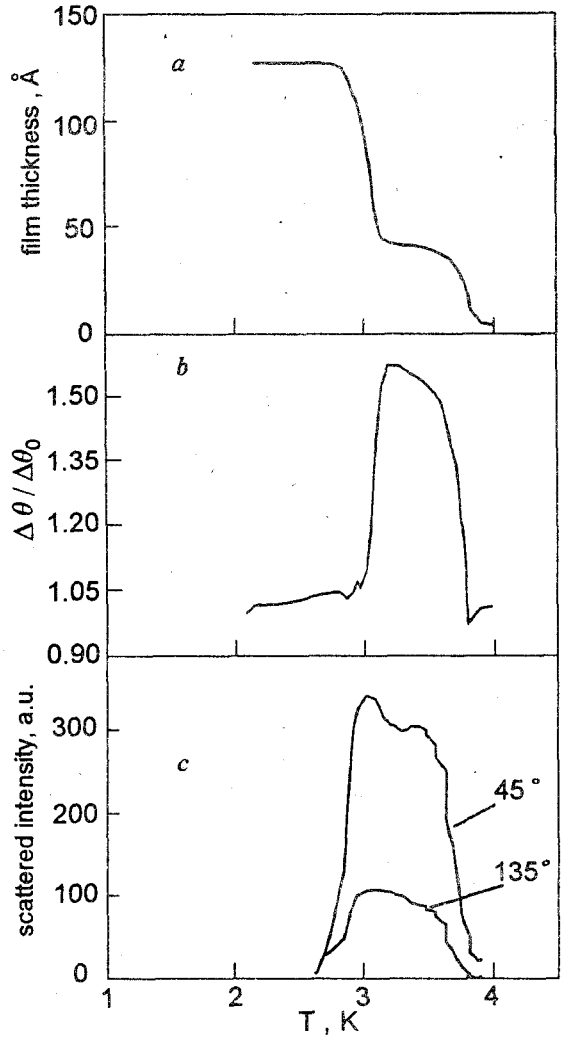

Fig. 7. Annealing of a quench-condensed H_2 film on Ag: *a*) effective thickness (determined from the SP resonance); *b*) reduced width of the SP resonance; *c*) scattered light intensity at two scattering vectors (45°: 3.7 μm^{-1}; 135°: 19.5 μm^{-1}). The temperature axis is simultaneously a time axis (1 K ≙ 1 h).

mons, so that the effective film thickness (i.e. the amount of material probed by the SP field) is reduced with respect to its initial value. The magnitude of this effect will of course depend on experimental parameters like the starting thickness and the annealing procedure. This was corroborated by a number of measurements under various experimental conditions. Although the details of the curves slightly changed, the essential features of Fig. 7 were always reproduced.

The model of coagulation in quench-condensed hydrogen films as a result of a dewetting process is

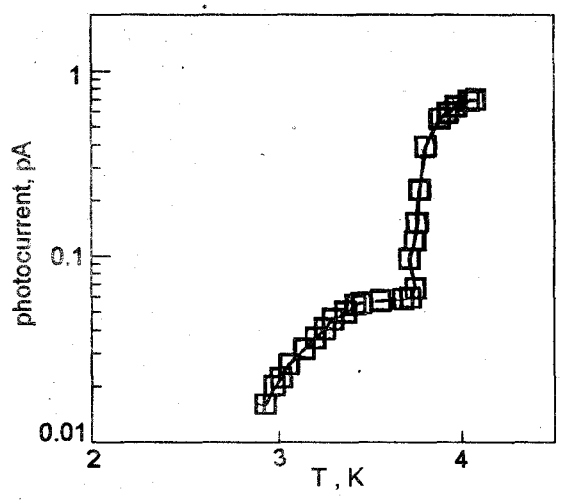

Fig. 8. Photocurrent from a silver film irradiated with UV light (photon energy ≈ 4 eV). Initially the silver was covered by a quench-condensed H_2 film (thickness ≈ 100 Å) grown at 1.5 K, and was then subjected to the same annealing procedure as the film in Fig. 7.

thus strongly supported. What is not yet clear on the basis of the data of Fig. 7 is whether the homogeneous film under the crystallites is in fact only a few monolayers thick, as expected for the incomplete wetting according to Fig. 4. The surface plasmon technique does not provide unequivocal information here. We have therefore used the photoemission of electrons as a complementary technique. As already described in Sec. 2, the photocurrent is drastically reduced by the presence of a hydrogen film. For a quench-condensed film on the order of 100 Å thickness it was far below our detection limit (see Fig. 8). During the annealing procedure beyond 2.8 K, however, the current recovered, and reached a plateau just as the signals in Fig. 7 before the desorption process led to another rapid increase. The observed difference in the photocurrent between the plateau region (~ 3.5 K) and the nearly free silver surface* (4 K) is close to a factor of 10, which is consistent with the presence of a roughly 10 Å thick homogeneous H_2 film after dewetting has taken place.

Whereas in the annealing experiments described so far the temperature was continuously increased at a constant rate, we have also made measurements where the temperature was quickly ramped up from the starting value T = 1.5 K to some final constant temperature T_a, where the sample was annealed and the relaxation towards the quasi-equilibrium state was recorded. Figure 9 shows this relaxation process

* The first H_2 monolayer is more strongly bound than the subsequent layers and desorbs only at higher temperatures.

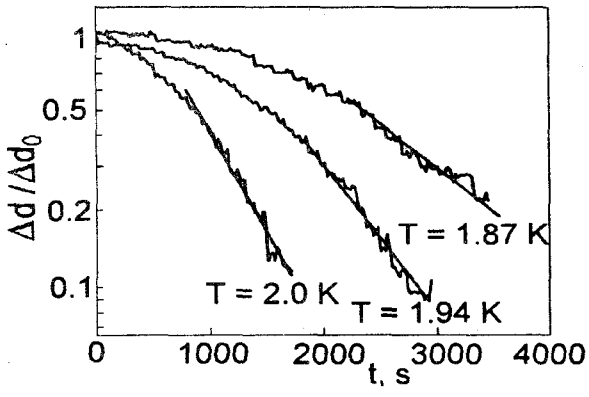

Fig. 9. Relaxation of the effective thickness of a quench-condensed H_2 film towards the quasi-equilibrium value at the plateau (c.f. Fig. 7,*a*, $T \geq 3$ K) for three annealing temperatures. Δd_0 and Δd are the differences between the thickness in the plateau state and the initial and the momentary effective thickness, respectively.

(here for the effective thickness) at three values of T_a. Obviously relaxation is visible in the effective film thickness already at significantly lower temperatures than suggested by the curve in Fig. 7,*a*, if the system has enough time to develop. A straight line in this semilog plot represents an exponential decay, and for each temperature a well-defined relaxation time τ can be determined. The τ decreases rapidly with increasing annealing temperature T_a. Our analysis yields an Arrhenius-like behavior, $\tau \propto \exp(-\Delta E/k_B T)$. The energy ΔE can be associated with the activation energy for surface diffusion. (The activation energy for *bulk* diffusion is so high that this mechanism is negligible in the temperature range considered here [11].) We obtain $\Delta E \cong 23$ K for the case of H_2, in close agreement with the value determined by Weiss and coworkers using surface acoustic waves [10].

The results, presented here mostly for H_2, hold in a similar way also for the heavier hydrogen isotopes. The characteristic temperatures are systematically shifted to higher values, as expected: the onset of diffusion, e.g., scales roughly in proportion to the square root of the isotope mass [6]. In general, our samples had the normal (room temperature) ortho/para ratio. Measures for conversion were not taken, but in some experimental runs, where the hydrogen had been stored at low temperatures for several days, a considerable increase in the fraction of para-H_2 should have occurred. Nevertheless, effects of the concentration of the ortho/para-species have not been found for the phenomena investigated here. Besides, the behavior of HD, which does not exhibit ortho-para-conversion, was also completely in line with H_2 and D_2.

5. Conclusions

In summary, this study of the wetting and surface transport properties of hydrogen films has shown that at low temperatures apparently a «zero-point-motion induced» surface-molten layer does not exist in these films. This implies that one intriguing possibility for surface superfluidity of hydrogen has infortunately also to be ruled out.

The incomplete wetting observed below the triple point is interesting in itself, but has also consequences for several other experiments with hydrogen films, as for example:

— Quench-condensed hydrogen films have been used as a substrate for electrons in vacuum surface states [12], which form unique 2*D* electron systems (like on liquid helium). For a high mobility of these surface state electrons the substrate surface should be as smooth as possible. Quench-condensed films are relatively rough and therefore are not ideal in this respect, and a smooth solid equilibrium film with a thickness of 100 Å or more would definitely be preferable. Yet, as the present investigations demonstrate, such a film cannot be prepared in equilibrium (at least not on the substrates used so far) due to the dewetting process.

— As a second example, thin quench-condensed films of molecular tritium are employed as a source in an experiment devised to determine the neutrino rest mass [13]. For that purpose, the spectrum of the electrons emitted in the β-decay of tritium is carefully measured in the vicinity of the end point energy, $E_{max} = 18.5$ keV. In order to keep unwanted energy losses of the electrons upon passage through the T_2 film small and, on the other hand, to have a reasonable count rate, the film thickness as a compromise is chosen around 10 monolayers. Such films, as shown here, are prone to coagulation. In fact, it has been found that when a film had been heated inadvertently so that bulk crystallites formed, the spectra were seriously distorted. One therefore has to take precautions that the tritium film, after condensation, is always kept at sufficiently low temperature (i.e. $T < 3$ K) so that surface diffusion processes are frozen out and coagulation cannot occur.

— Triple point wetting with its rapid variation of the film thickness just below T_3 can easily affect experiments with hydrogen in films or also in porous media like grafoil or vycor glass, when in contact with the vapor space. Dewetting therefore should always be taken into account as a possible source for spurious signals, in particular near T_3. In porous media, the dewetting process can be shifted somewhat in temperature compared to free films due to finite size effects.

Finally, since the wetting behavior is determined by a delicate competition between adsorbate-adsor-

bate and adsorbate-substrate forces, one can imagine that for some substrates — including perhaps more complex, multilayer systems — hydrogen *will* exhibit complete wetting even below the triple point temperature. This would allow growing well-ordered hydrogen films with distinctly larger thickness that only a few monolayers as on the «ordinary» surfaces studied here. For a number of applications such films would be of great interest.

Acknowledgements

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