

Investigation of Quantum Systems with Surface Plasmons and Surface State Electrons

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We report on investigations of thin films of the quantum systems hydrogen and helium both in thermodynamic equilibrium and in metastable states. Information about the film thickness and surface roughness is obtained from the excitation of surface plasmons and mobility measurements of surface state electrons. The equilibrium studies show triple-point wetting for H₂ on Au substrates, in agreement with earlier results for similar systems. Unexpectedly a distinct hysteretic behavior of the saturated film thickness is found near the triple-point. Superfluid ⁴He films on as prepared Ag display complete wetting. Investigations of H₂ films in metastable states prepared by quench-condensation at 1.5K reveal pronounced changes in the film structure upon annealing. These changes set in far below the desorption temperature and are ascribed to surface diffusion.

1. INTRODUCTION

Surfaces of the quantum systems helium and hydrogen provide a large variety of interesting problems. Unfortunately many of the sophisticated techniques which have been developed for investigating surface and interfacial properties of classical systems are not applicable here because of the necessary low temperatures or the relatively high vapor pressure of the condensed phases to be studied. In this paper we describe two methods based on surface plasmons and surface state electrons which have turned out to be well suited for investigating surface phenomena of quantum sys-

tems; mainly thin films of hydrogen (and its isotopes) and helium will be discussed.

Hydrogen films can be prepared both in equilibrium and in nonequilibrium, metastable states, because at low temperature the diffusion coefficient in the solid phase is very small. Helium films, on the other hand, being liquid down to the lowest temperatures (apart from the first one or two monolayers) are generally in a state close to thermodynamic equilibrium. A typical equilibrium property is the wetting behavior, which is the topic of section 3. An example for systems far from thermodynamic equilibrium are quench-condensed solid films, whose annealing behavior is discussed in section 4.

2. EXPERIMENTAL

Surface state electrons (SSE) as a probe for the surface properties of quantum systems have been treated already in several reviews¹ and will therefore be described only briefly here. The method is based on the fact that the electrostatic image potential for electrons above the condensed phases of hydrogen, helium and neon is very small due to the low polarizability of these substrates. The electrons are therefore bound perpendicular to the surface in external surface states at a relatively large average distance from the surface, which for electrons in the ground state amounts to slightly above 100Å for ⁴He and about a factor of 5 less for H₂. This gives rise to a high electron mobility parallel to the surface, restricted mainly by scattering from gas atoms, surface excitations like ripplons and also static surface irregularities. Due to the latter mechanism the electron mobility therefore provides information about the surface roughness.

The second method, surface plasma resonance, is well known as a very sensitive technique for investigating surfaces and adsorbed films², and to our knowledge is applied here to quantum systems for the first time. In our experimental setup we use the so called Kretschmann configuration³ (for details see ref.4): The surface plasmons (SP) are excited in a thin metal film (in our case Au or Ag) on a glass prism, which is illuminated by a parallel beam of monochromatic light. By varying the angle of incidence θ , one can match the component of the photon wavevector parallel to the surface to the wave vector of the surface plasmons at the laser frequency. At resonance the incident photons couple very efficiently to the surface plasmons, so that the reflected light intensity at that particular angle θ_R is strongly reduced. 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 of the order of the wavelength of light) this shift is linear in d , with

$$d = C(p)(\theta_R(d) - \theta_R(0)) , \quad (1)$$

where p is the polarizability of the adsorbed molecules, which enters the

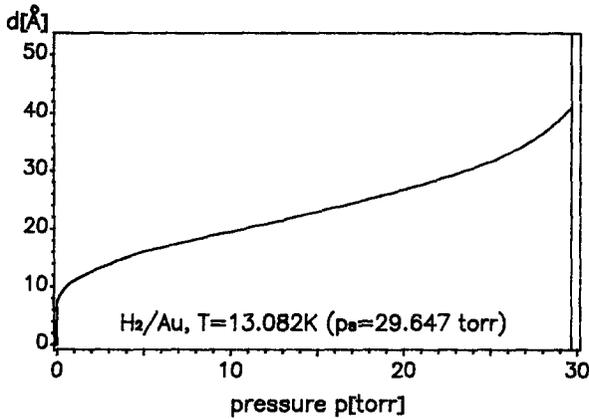


Figure 1: Adsorption isotherm of H_2 on a gold substrate at $T=13.082K$.

prefactor $C(p)$. From this it is possible to determine the absolute (optical) thickness of the adsorbate. In addition, a possible roughness of the adsorbed film shows up as an increase of the SP resonance width $\Delta\theta$.

Although a quantitative analysis in terms of surface roughness still requires more detailed theories both for SSE and for SP, the experimental data on electron mobility and plasmon width can nevertheless be used to follow changes in the surface structure as they develop, e.g., during annealing procedures or the layered growth of liquid helium films.

3. WETTING BEHAVIOR

A central aspect of physisorbed films is the question whether complete or incomplete wetting occurs, i.e. whether in thermodynamic equilibrium the film thickness diverges or remains finite when the system approaches the saturated vapor pressure. This is determined by a subtle balance between the interaction among the adsorbate molecules and the adsorbate-substrate interaction. The degree of wetting in general depends on temperature, which can lead to phase transitions from incomplete to complete wetting. For simple systems this transition is frequently found to take place at the triple-point⁵.

Motivated by these earlier experiments we have used SP to study the wetting behavior of hydrogen and neon adsorbed on a gold substrate (the gold surface was exposed to the atmosphere before being mounted in the sample cell and therefore was probably covered with a layer of water) in the vicinity of the triple-point. An example for an adsorption isotherm of H_2 (normal ortho-para mixture) is shown in fig.1 for $T=13.08K$, $0.88K$ below the triple-point. Obviously the solid hydrogen film only grows up to a maximum thickness d_s at saturated vapor pressure, 40\AA in this case, implying that H_2 does not wet the substrate completely at that temperature.

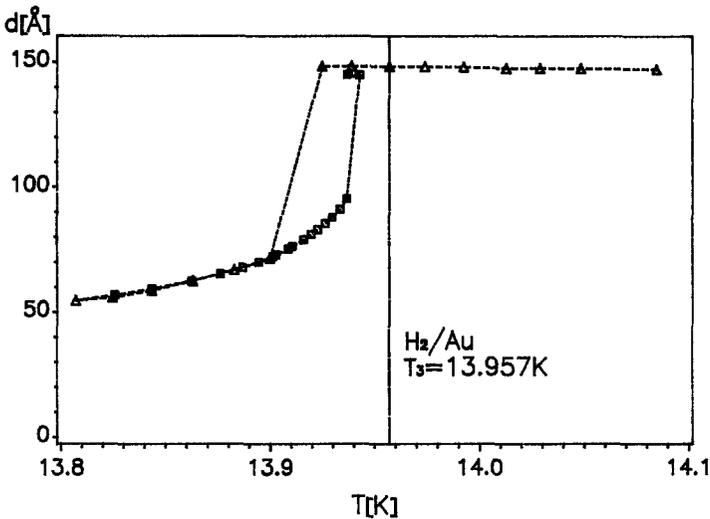


Figure 2: Film thickness d_s at saturated vapor pressure vs. temperature. The triangles were taken on cooling, the squares on heating.

If excessive gas is added, it condenses in bulk crystallites at the bottom of the sample cell, the film thickness remaining at d_s .

In order to determine the temperature dependence of this maximum thickness we filled the sample cell with a sufficient amount of hydrogen, so that the film was always in coexistence with bulk phase at the cell bottom. When the temperature was changed, the film thickness relaxed towards its new value within a time shorter than the time constant of the electronics of about 5 sec. A representative run, shown in fig.2, started above the triple-point, where d_s is independent of temperature*. As the temperature was decreased below the triple-point, the film thickness suddenly dropped and then reversibly followed the solid curve. Upon increasing T above 13.94K again a discontinuous jump was observed, this time up to the saturation value of 150Å.

For an interpretation of the critical behavior we have plotted in fig.3 the variation of d_s , given by the solid line in fig.2, vs. the reduced temperature $t = (T_3 - T)/T_3$ (the correction in T due to the temperature gradient mentioned before is taken into account here). The data can apparently be represented well by a power law $d_s \sim t^{-\alpha}$ with $1/\alpha = 3.00 \pm 0.04$, which is exactly the value expected for systems with van der Waals-interaction, and has been found similarly also for other adsorbate-substrate combinations⁵.

* For triple-point wetting one would expect d_s to diverge in this temperature range, if the film is in thermodynamic equilibrium with the bulk phase. The observed finite thickness is probably due to a small temperature gradient in the sample cell; a temperature difference of 8mK between the film and the bulk phase⁶ can account for a reduction of d_s to the measured value of 150Å.

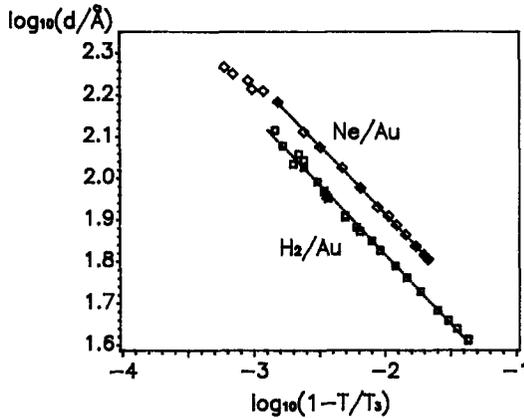


Figure 3: Film thickness d_s vs. the reduced temperature (with respect to the triple point temperature T_3). The dashed lines represent a behavior $d \sim (1 - T/T_3)^{-1/3}$.

Although in that respect the agreement with existing theories for triple-point wetting appears to be quite satisfactory, the observed hysteretic behavior near T_3 is in striking conflict with the idea that the phase transition from incomplete to complete wetting at T_3 is of second order. Certainly more detailed measurements are required to exclude experimental artifacts. On the other hand it would not be too surprising if the existing theories fell short of explaining the actual behavior close to T_3 , because important features of the system, e.g., the formation of a surface-molten layer on the solid film below T_3 have still to be taken into account.

Qualitatively the same behavior as for hydrogen is also found for neon on a gold substrate. Also in this case hysteresis is observed. The critical exponent α is again very close to $1/3$ (see fig.3); deviations for thick films can be attributed to retardation effects.

We have also studied the wetting behavior of ^4He films, for which quite controversial results exist in the literature⁷⁻¹⁰. The substrate for exciting the surface plasmons in this case was Ag (again covered with a thin water film as in "usual" low temperature experiments), and the measurements were restricted to temperatures below T_λ . The resulting adsorption isotherms (an example is given in fig.4) show a continuous growth of the film thickness up to 25 monolayers and are consistent with complete wetting. An indication for incomplete wetting with a limiting thickness d_s of only a few monolayers⁷ was not found.

4. ANNEALING OF QUENCH-CONDENSED FILMS

According to the data presented in the previous section the maximum equilibrium thickness of H_2 films far below T_3 should only be a few monolayers.

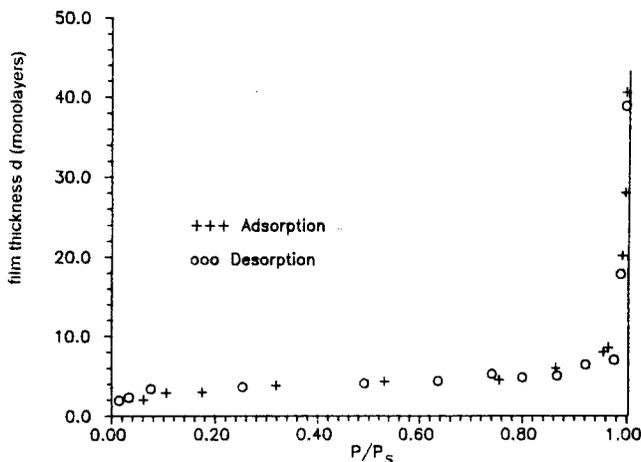


Figure 4: Adsorption isotherm of ^4He on Ag at a temperature of 1.738K (saturated vapor pressure $p_s = 9.93\text{ torr}$).

Metastable disordered films, however, can be grown to much larger thickness by means of quench-condensation. We have studied the relaxation behavior of such films in annealing experiments using again surface plasmons and, in addition, surface state electrons.

Experiments with surface plasmons. The films were prepared by quench-condensation onto a silver surface at about 1.5K, the gas entering the cell had a temperature below 25K. The growth of the films was again monitored via the shift of the SP resonance angle using eq.1. The width of the SP signal, which was recorded simultaneously, showed no broadening as compared to the bare silver surface, hence the adsorbed films were smooth and homogeneous on an optical length scale. The subsequent annealing was performed at a rate of 0.5K/h for the experiments shown below. Measurements at slower rates proved the results to be qualitatively independent of the annealing rate. Since these experiments were carried out in an "open" cell, i.e. all material desorbing from the surface was pumped away with a cryopump, recondensation from the gas phase did not occur.

In fig.5a we have plotted the result of an annealing experiment for a quench-condensed H_2 film with an initial thickness of 93\AA . The shift in θ_R (plotted as optical thickness d , assuming bulk density) and the resonance width (normalized to the value on bare silver) are plotted vs. the annealing temperature. Below about 2.6K both signals are constant and show no indication of annealing effects. Between 2.6 and 2.8K, however, there is a strong increase in SP scattering, accompanied by a drastic shift of d to about half its initial value. Above 2.8K the values of both d and θ_R again remain approximately constant, until eventually desorption sets in around 3.5K.

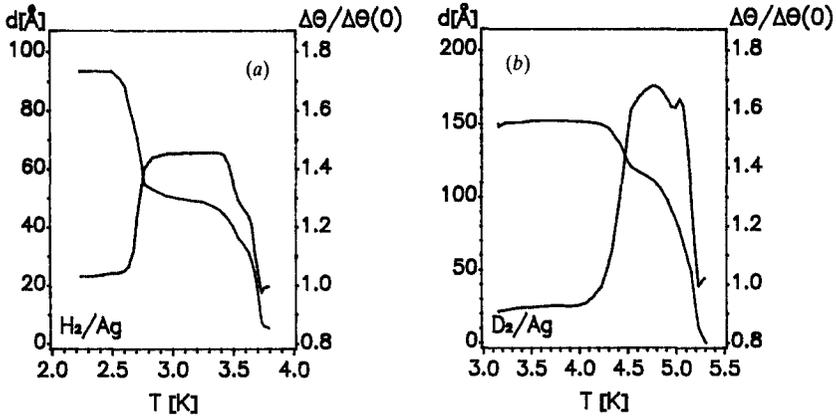


Figure 5: a) Annealing behavior of a quench-condensed H_2 Film. d is the apparent thickness (determined from the SP resonance, full line), $\Delta\theta/\Delta\theta(d=0)$ is the normalized SP width (dashed line), and T is the annealing temperature. b) Same as a) for D_2 .

The same characteristic behavior with a transition to an intermediate state, though less pronounced, is found also for films with a thickness of only a few monolayers. It is similarly observed for films of the hydrogen isotopes HD and D_2 (fig.5b); the transition occurs there around 3.7K and 4.3K, respectively. By contrast, quench-condensed Neon films do not exhibit any significant change in d and $\Delta\theta$ up to the desorption temperature (see fig.6).

The crucial point in interpreting the observed annealing behavior is the pronounced decrease in d . This can be caused either by a real loss in coverage or by a drastic rearrangement of the molecules in the film, that would position a substantial number of them at a large distance from the silver surface, where θ_R is not a linear function of the film thickness anymore ($d > 1000\text{\AA}$). A considerable loss in coverage seems rather unlikely well below the bulk desorption threshold. We thus suggest that our observations are indicative of the formation of crystallites with sizes on the order of the light wavelength, which occurs as a consequence of incomplete wetting. This would also explain the strong scattering of the SP waves. Since bulk diffusion so far below the triple-point temperature should be negligible¹¹, diffusion at the surface appears as the only possible mechanism for such a large scale rearrangement of the hydrogen molecules.

Experiments with surface state electrons. SSE have been shown to be a very sensitive probe for studying the surface of bulk quantum systems¹. We have therefore tried to use them also for characterizing the annealing of quench-condensed films, because the electrons, compared to SP, probe the surface on a smaller length scale. Unfortunately, H_2 films with an initial thickness of some 100\AA , as described above, turned out not to be

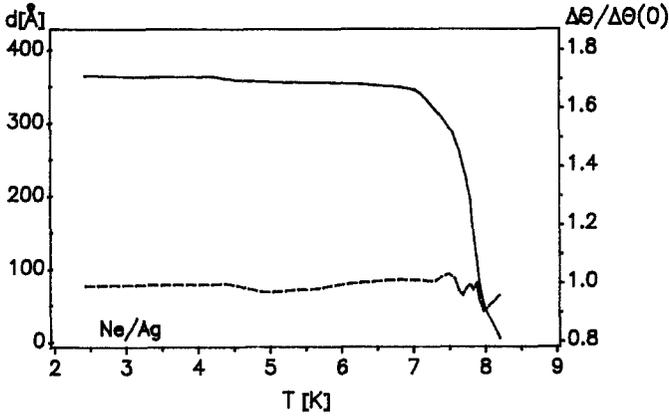


Figure 6: Apparent thickness and reduced SP width of a quench-condensed Ne film vs. the annealing temperature T .

accessible with this method: Electrons are not stable on these films, but penetrate them rather easily. Since tunneling over such large distances is very unlikely, this indicates that these films are not compact, but have a porous structure¹², which allows the electrons to pass to the substrate.

We found, however, that on thicker ($d \sim 1 - 2 \mu\text{m}$) quench-condensed H_2 films electrons can be trapped over an extended period of time¹³. Directly after the condensation process at $T < 1.8\text{K}$ the disorder of the films was so large that the SSE conductivity σ was below our detection limit (fig.7). Raising the temperature to 3.5K resulted in a measurable signal of σ , which could be further increased by several orders of magnitude by annealing at still higher T (these measurements were performed in a "closed" cell, where the film was in equilibrium with its vapor, hence annealing up to 8K was possible without losing the film.). After annealing the conductivity shows a weak variation with temperature at high T and an exponential drop at low T , which we interpret as a thermally activated motion of the electrons in a surface potential with reduced, but still noticeable disorder. The activation energy could be successively reduced by subsequent annealing steps¹³. The at first sight contradictory result that annealing enhances the scattering of SP, whereas on the other hand it improves the conductivity of SSE, can be attributed to the different length scales on which the two probes are sensitive.

These measurements so far are preliminary, and more systematic investigations are necessary for a better understanding of the annealing behavior of quench-condensed films. Still the results show that H_2 films appear as a promising system for further investigations. As an example fig.8 shows the SSE conductivity on a hydrogen film in the presence of ^4He . The modulation in σ is caused by layering of the ^4He film, which for helium on bulk H_2 substrates has already been reported earlier^{14,15}. The observed

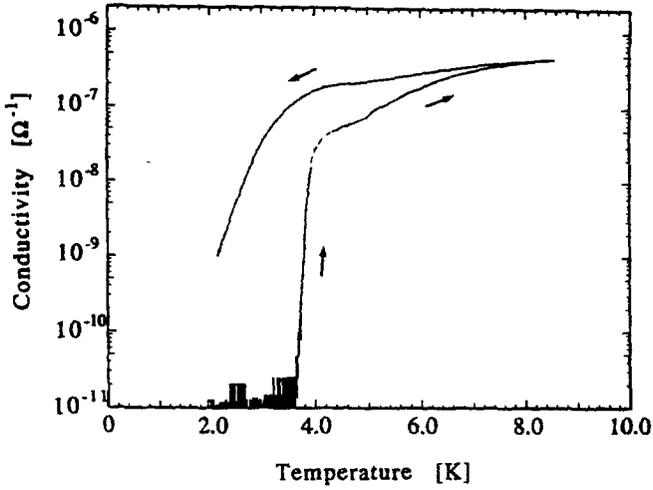


Figure 7: Behavior of the SSE conductivity σ during the first annealing process after the quench-condensation of the hydrogen substrate. Arrows indicate the direction of the chronological development.

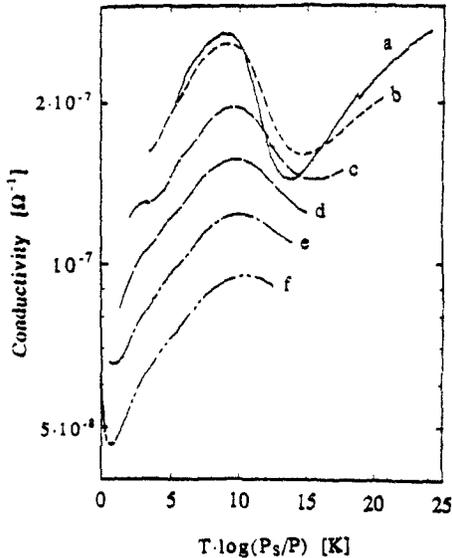


Figure 8: SSE conductivity on a hydrogen film, plotted vs. the chemical potential $T \log(p_s/p)$, where p_s is the saturated vapor pressure of helium and p is the actual pressure of helium in the cell. Labels (a)- (f) correspond to different helium gas atom densities: (a) 0.51; (b) 1.1; (c) 2.4; (d) 4.6; (e) 6.7; (f) $9.7 \times 10^{19} \text{ cm}^{-3}$.

conductivity maxima at a chemical potential of 9K (with respect to the bulk liquid) can be associated with the completion of the first ^4He monolayer. This demonstrates the good surface quality that can be achieved with quench-condensed hydrogen films, which, in addition to the various aspects of physisorption addressed here, makes them an interesting substrate for studying 2-dimensional electron systems.

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