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Structural Stability of Solid Deuterium Films

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The wetting behavior of quenched-condensed solid D_2 films has been investigated by means of light scattering. On the substrates used here (graphite and aluminum) molecular deuterium displays triple point wetting and hence dewets in the solid state, provided the temperature is high enough that thermally activated diffusion processes can take place. This manifests itself in a coarse-graining of the D_2 film. In order to avoid this process and to obtain complete wetting of solid D_2 we have modified the adsorbate-substrate interaction potential by preplating the substrates with thin inert layers of Ne, Ar, CH_4 or C_2H_6. The predicted change in the wetting properties was not observed, however, suggesting that the existing picture of triple point wetting of van der Waals systems is not complete. The implications of these results for a neutrino mass experiment where quenched-condensed molecular tritium films are used as a source are discussed.

I. INTRODUCTION

Molecular hydrogen and its isotopes, due to their filled electron shell, are only weakly polarizable and interact essentially via van der Waals forces. The physisorption of these molecules on solid surfaces might therefore be expected to be a rather simple phenomenon. As it turns out, however, the formation of homogeneous hydrogen films poses considerable problems, at least in the solid phase. Molecular hydrogen exhibits the effect of triple point wetting, which implies that although liquid films above the triple temperature T_t can grow to arbitrary thickness, solid H_2 well below T_t in thermal equilibrium forms only films of at most several monolayers.[1, 2] This hampers the use of solid H_2 films for potential applications as well-defined matrix or substrate material. Experiments where homogeneous and smooth films of solid hydrogen isotopes would be quite useful cover such different areas as optical spectroscopy, laser fusion, studies of two-dimensional electron systems and the determination of the neutrino rest mass.[3, 4] It is the last of these examples which motivated the research reported here.

A possible approach for a determination of the rest mass of the neutrino (more exactly: the electron antineutrino) is based on the β-decay of tritium. In such an experiment the energy spectrum of the beta particles in the vicinity of the end point energy (18.6 keV for tritium) has to be measured with high accuracy. For that reason the choice of a proper tritium source is rather critical, because the beta electrons should interact so weakly with the source material that most of them suffer no energy loss before leaving the source. In the neutrino experiment carried out at the University of Mainz a frozen film of molecular tritium is used, which satisfies this condition as long as the film is only some ten nanometers thick and homogeneous.[4, 5]

The latter requirement, however, is not easily achieved: As mentioned above, *equilibrium* films of hydrogen isotopes in the solid state reach only a thickness of a few monolayers, which at a given source area of about 1 cm^2 is too little T_2 material to yield a reasonable beta count rate. Although thicker films can be prepared by quench condensation of T_2 vapor on a substrate which is kept at sufficiently low temperature (a method actually applied so far for the T_2 source in Mainz), the problem there is that these films tend to dewet, since they are not in a thermodynamically stable state. If they slightly warm up—even only for a short time—so that surface diffusion can set in, clusters up to micron size form[6] which are far too large to be acceptable considering the energy loss of the beta particles.[7] The dynamics of this process and its dependence on temperature and hydrogen isotopes were extensively studied.[8–10]

In the experiments described here we have therefore tried to reach a regime where the adsorbed films display complete wetting instead of triple point wetting and thus should be intrinsically stable. According to theoretical considerations[11] this should be possible by modifying the interaction between the solid substrate and the films by preplating the substrate with proper materials. As will be shown, however, this strategy did not work out: For all the material combinations we investigated we observed dewetting of the films. Although the study was not successful in this respect, the results are interesting from a general point of view because they suggest that the existing models for triple point wetting might not be complete.

The measurements reported here were carried out with D_2 instead of T_2, because tritium is much more problematic to handle than deuterium. Since the Lennard-Jones parameters of the various hydrogen isotopes are quite similar, however, the results obtained here should be applicable also to tritium, if the difference in mass and its influence on activation energies, diffusion etc. are taken into account.[8, 9, 12]

II. THEORETICAL BACKGROUND

The interaction between a hydrogen molecule and all other materials (except for some "pathological" cases like helium and cesium[13] is stronger than the interaction among the hydrogen molecules themselves. Thus according to simple arguments hydrogen ought to exhibit complete wetting on "conventional" substrates. Experimentally this is true, however, only for the liquid phase, as already indicated. A possible origin for the lack of complete wetting in the solid state of such weakly bound films has been pointed out already some time ago by Gittes and Schick (GS).[11] The essential parameter in this theory is the relative substrate strength *R*, which describes the effective interaction between the substrate and the adsorbate as it is calculated from a combination of the van der Waals constants of the involved media (see Fig. 1). If the substrate strength is low ($R < 1.8$), incomplete wetting should occur, because the cohesion energy within the adsorbate outweighs the adsorption energy to the substrate, which makes it unfavorable to grow a thick film (this holds both for liquid and solid films). At high values of *R* (>3), on the other hand, one expects again

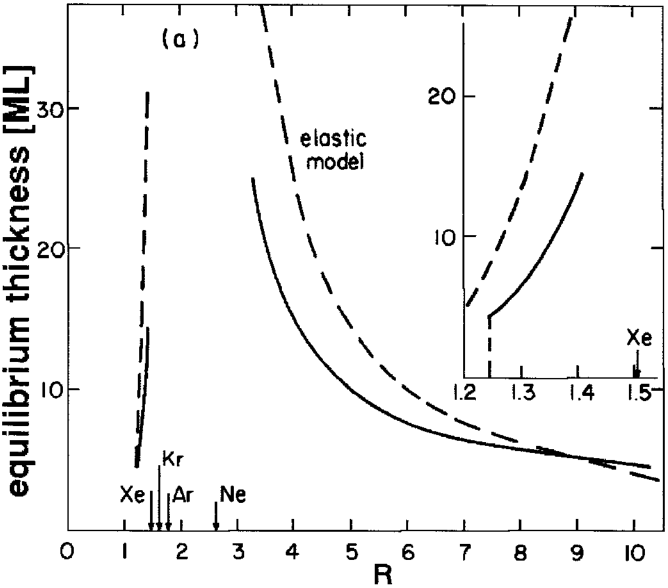

Fig. 1. Equilibrium layer number of various van der Waals films at saturated vapor pressure adsorbed on graphite vs. integrated potential strength *R*, as calculated by Gittes and Schick (taken from Ref. 11). Solid lines are the interpolated results of microscopic calculation, dashed line is the result of elastic calculation.

TABLE I

Relative Substrate Strength *R* Calculated for Various Substrate Materials and H_2 as Adsorbate

Substrate	Ne	Ar	CH_4	C_2H_6	Al	Graphite
R	0.92	2.13	2.05	2.51	5.64	8.20

incomplete wetting, but now due to deformation and strain of the adsorbate (as long as the film is solid) under the influence of the strong attractive forces of the substrate. As it was shown by GS this effect is not simply related to a lattice mismatch between substrate and adsorbate, but it persists also if a strong, yet structureless substrate is assumed. As a general result, therefore, only in a small range of substrate strength, $1.8 < R < 3$, is complete wetting to be expected (cf. Fig. 1).

On the basis of this theory we have calculated the relative substrate strength for various substrate materials (see Table I). For the two substrates used in this work, aluminum and graphite, the resulting values of *R* are far above the range where complete wetting is to be expected. This should change, however, when the substrates are preplated with thin cryogenic films, and it should be possible to tailor the effective substrate strength *R* in such a way that it falls into the range of complete wetting. Preplating with Ne, e.g., allows the largest variation of the effective substrate strength, since Ne is the weakest substrate for hydrogen listed in Table I. Yet, if the thickness of the Ne layer gets too large, *R* should drop below the stable range $1.8 < R < 3$, and incomplete wetting should prevail again. Less critical in this respect are Ar, CH_4, and C_2H_6 as preplating materials. There even for very thick preplating layers the value of *R* should remain in the regime where according to Fig. 1 complete wetting is to be expected.

In a preliminary measurement it was indeed observed[2, 14] that on a silver substrate preplated with Ne hydrogen films could be grown to a distinctly larger thickness than on the bare metal. It was the aim of the present work to study this behavior in a more systematic way, and under conditions adequate for the neutrino mass experiment.

III. EXPERIMENTAL

In order to investigate the development of the physisorbed films in our experiment we used the set-up sketched schematically in Fig. 2. The thickness of the adsorbate was determined by means of ellipsometry, while light

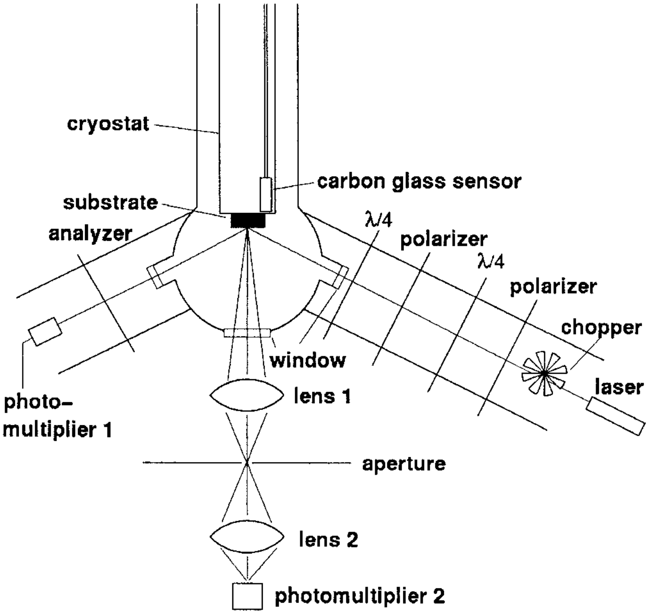

Fig. 2. Experimental set-up for investigating quench-condensed deuterium films. Photomultiplier 1 registers the ellipsometer signal and thus the film thickness, photomultiplier 2 the stray light resulting from the film roughness. The first polarizer-$\lambda/4$ combination in the laser beam is used for generating circularly polarized light. For further details, see text.

scattering provided information about the roughness of the film and hence the dewetting process.

The ellipsometer consisted of a usual PCSA (polarizer/compensator/sample/analyzer) configuration. Due to the non-ideal quality of our substrates the thickness resolution was somewhat limited, but still allowed to detect changes in the adsorbate on the order of a monolayer, which was completely sufficient. Through a separate window we collected the light scattered by the sample roughness (mainly due to the adsorbed film, but also with some background from the substrate) and focused it onto a photomultiplier by means of two lenses. An aperture served to eliminate stray light from the windows and cell walls. A He–Ne laser ($\lambda = 633$ nm, 1 mW) was used as a light source, and the laser beam was modulated by a chopper in order to allow for lock-in detection of the scattered light.

The preferred substrates used in the Mainz neutrino mass experiment so far were highly oriented pyrolytic graphite (HOPG) and aluminum because of their small cross section for electron backscattering. These substrates were therefore also chosen for the present measurements, either in the form of an evaporated film (Al) or as a platelet (HOPG) glued onto the cold finger of the cryostat. Since the thermal conductivity of HOPG perpendicular to its surface is rather poor and moreover the thermal contact to the cold finger may vary, the temperature at the surface of these samples can deviate from the one measured at the cold finger (by means of a carbon glass thermometer). In order to obtain information about this temperature difference we have at the end of each run, when the film was desorbed, measured the desorption rate (which via the vapor pressure of the adsorbate is directly related to the film temperature). The temperature difference ΔT between sample surface and cold finger determined in this way amounted to 0.2 up to 0.5 K. For the aluminum substrates, ΔT was negligible within our accuracy of about 0.1 K.

The deuterium films were condensed at typical rates around 10 nm/min, with the substrate temperature being kept fixed at values between 1.6 and 2.5 K. The temperature of the condensing gas could not be measured, but since the feeding capillary was only cooled at its end due to radiation cooling, we assume that it was at least as high as 20 K or even higher.

After the preparation of the film the shielding cap positioned in front of the substrate during the condensation[10] was removed, so that optical access to the sample through the cryostat window was established, and the scattered light could be collected. In the next step the substrate temperature was increased to a value where the relaxation process of the film was to be studied. The intensity of the scattered light, which gives a measure of the developing film roughness upon annealing, was then registered as a function of time. Once the relaxation process had come to an end, the substrate temperature was increased further so that the D_2 film desorbed, and the background scattering due to the substrate (including possible preplating layers) could be determined. A comparison with the scattering signal at the beginning allowed then to draw conclusions about the existence of scattering centers in the as-quenched film, like porosity and larger defects.

IV. RESULTS AND DISCUSSION

In Fig. 3 we have plotted the scattered intensity as a function of time for one of such runs. The lower trace shows the corresponding temperature of the substrate (The temperature difference ΔT to the cold finger was 0.4 K in this run.) The sample consisted in this case of HOPG, preplated by a layer of 3.3 nm Ar (quench-condensed at a temperature of 2 K) and covered by a 13 nm thick D_2 film prepared by quench-condensation at 2.1 K. At $t = 250$ s the temperature of the substrate was raised to 4.4 K, a temperature sufficiently high that surface diffusion of D_2 allows a relaxation of the film towards its equilibrium state. As the figure shows, a pronounced increase of the scattered intensity is observed, which can be ascribed to the roughness due to crystallites which grow during this annealing stage. The relaxation process takes about 1800 s under the given conditions. The slow decrease afterwards is probably due to a slow desorption of D_2 molecules, which at 4.4 K is already noticeable, and which leads to a gradual shrinkage of the scattering centers. Eventually, at $t = 4600$ s the substrate temperature was increased to $T > 7$ K, giving rise to an essentially instantaneous and total desorption of the D_2 film. As seen in Fig. 3, the intensity of the scattered light drops then back to its initial value with the as-quenched D_2 film. This implies that any roughness of this film in the beginning of the run had been on a length scale small compared the wavelength of the incident light, because it did not give rise to noticeable light scattering.

The increase in film roughness upon annealing, as it follows from Fig. 3, is a clear indication that a preplating layer of 3.3 nm Ar on HOPG does

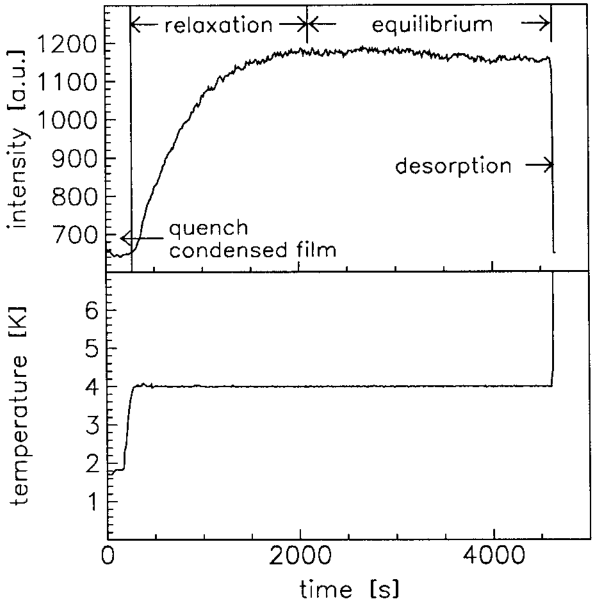

Fig. 3. Light intensity scattered from a D_2/Ar film on Graphite as a function of time (upper trace). The lower trace shows the corresponding temperature as measured with the carbon thermometer; the sample temperature was about 0.4 K higher in this run. The D_2 film was prepared by quench condensation at 2.1 K. At $t = 250$ s the temperature was increased to the annealing stage ($T = 4.4$ K), and at $t = 4600$ s the D_2 was desorbed.

not qualitatively change the wetting behavior of the D_2 film, in contrast to what we had expected on the basis of the data of Table I and Fig. 1. In order to make sure that this result was not just caused by an unfortuitous choice of experimental parameters, we carried out a careful investigation with a large variety of different samples, changing preplating materials, film thicknesses and also substrates. All these runs, however, as they are listed in Table II, resulted in qualitatively the same curves as in Fig. 3. Also the relaxation times for the dewetting process with and without preplating were of the same order of magnitude (in general preplating resulted in somewhat shorter times, but systematic studies have still to be carried out). From these observations we have to conclude that even in the presence of

TABLE II

Combinations of Substrates, Preplating Layer Material and Thickness, and D_2 Film Thickness Investigated in this Study. The Last Column Indicates whether Relaxation Towards a Coarse-Grained D_2 Film was Observed. As the Entries Show, no Combination Without Coarse-Graining was Found

Substrate	Preplating	Film	Relaxation
graphite	11 Å Neon	138 Å D_2	yes
graphite	18 Å Neon	111 Å D_2	yes
graphite	38 Å Neon	113 Å D_2	yes
graphite	54 Å Neon	130 Å D_2	yes
graphite	142 Å Neon	122 Å D_2	yes
graphite	145 Å Neon	131 Å D_2	yes
graphite	177 Å Neon	112 Å D_2	yes
graphite	6 Å Argon	128 Å D_2	yes
graphite	11 Å Argon	120 Å D_2	yes
graphite	23 Å Argon	118 Å D_2	yes
graphite	23 Å Argon	121 Å D_2	yes
graphite	33 Å Argon	130 Å D_2	yes
graphite	105 Å Argon	120 Å D_2	yes
graphite	13 Å CH_4	130 Å D_2	yes
graphite	21 Å CH_4	119 Å D_2	yes
graphite	44 Å CH_4	128 Å D_2	yes
graphite	18 Å C_2H_6	124 Å D_2	yes
graphite	45 Å C_2H_6	121 Å D_2	yes
graphite	99 Å C_2H_6	129 Å D_2	yes
aluminum	15 Å Argon	134 Å D_2	yes
aluminum	36 Å Argon	158 Å D_2	yes
aluminum	73 Å Argon	123 Å D_2	yes
aluminum	120 Å Argon	141 Å D_2	yes
aluminum	208 Å Argon	133 Å D_2	yes

preplating layers—and hence markedly changed van der Waals interaction of the D_2 molecules with the substrate—could the roughening of the film in the annealing stage not be suppressed, suggesting that in contrast to the ideas presented in Sec. II complete wetting of the solid film was not achieved.

This obviously raises the question for the origin of this discrepancy. One serious difference between the conditions of our experiment and the model of Gittes and Schick is that in the latter homogeneous and smooth surfaces are assumed, whereas the preplating films in our measurements probably have inhomogeneous, porous structures, as they generally appear for quench condensation of Lennard-Jones systems.[16] This might give rise to local strains, which could override the subtle effect of tailoring the van der Waals interaction by preplating. Besides, pores in the preplating film would reduce the effective van der Waals interaction and therefore require a modification of the calculated values of R_{eff} in Table I. (Since a large variety of different samples has been studied, however, it is not very likely that in this way one would always have missed the stability range of complete wetting as displayed in Fig. 1.) In addition, one might also argue that the inhomogeneities of the substrate and the preplating layers provide a host of nucleation sites for crystallites with different orientation, thus preventing the formation of a homogeneous solid D_2 layer.

The porosity of quench-condensed films is known to depend in its details strongly on the preparation conditions, in particular on the kinetic energy of the gas molecules as they condense on the cold substrate. The higher the temperature of the arriving molecules, the more compact is the structure which forms.[16] It has been observed already earlier that the relaxation time of the dewetting process is distinctly increased for such compact hydrogen films,[9, 15] which is plausible because diffusion processes will be more suppressed in the denser structures. It might well happen, therefore, that under favorable preparation conditions a film becomes so closely packed during quench condensation that, although not being in a thermodynamically stable state, it appears to be stable on the time scale of the experiment. This could also be the origin for the difference in the behavior found here and in the preliminary, promising experiments by Conradt *et al.* mentioned in Sec. II.

At this stage we unfortunately do not have a sufficiently complete characterization of our films that these points could be discussed in any detail, and more work has certainly to be done to clarify the situation. We would like to mention, though, that in complementary measurements with molecular hydrogen films, which have been carried out near the triple point, a similar lack of influence of preplating on the wetting behavior has been observed.[17] Since those experiments were done with both hydrogen and preplating layers adsorbed close to thermodynamic equilibrium, most of the arguments given above regarding the frozen-in disorder in the films do not apply there. Thus the present picture of triple point wetting on real substrates might not be complete after all.

V. CONCLUSIONS

From the practical side, the main result of our study is that preplating is obviously not a proper strategy to prepare van der Waals films which are resistant to coarse graining. Another relatively simple method, however, which we discovered in the course of our experiments, allows to suppress the formation of larger (i.e., comparable to the wavelength of light) crystallites upon annealing quite efficiently: If the original quench-condensed D_2 film—even without preplating layer—is covered by just roughly a monolayer of heavier adsorbate like Ar, it withstands annealing up to the evaporation temperature without showing the characteristic increase in light scattering which is indicative of film roughening. A straightforward explanation for this phenomenon is that the Ar layer, due to its much higher activation energy for surface diffusion, also suppresses diffusion processes at the surface of the D_2 film, and thus provides a kinetic barrier for the coarse graining process. For practical applications, this is an interesting alternative to the other possibility to avoid roughening of quench-condensed hydrogen isotope films, namely keeping the temperature of the film always sufficiently low that surface diffusion is frozen out (which is also simple in principle, but in some experiments difficult to fulfil).

Finally, as it comes to the consequences of the present results for the stability of T_2 films in the neutrino experiment, one might argue that the study of D_2 for that purpose is in any case of only limited value because of the radioactivity of the tritium. It was supposed, e.g., that the energy transferred from a decaying nucleus to the surrounding lattice could locally heat the film so strongly that dewetting cannot be suppressed even for very low substrate temperatures. As the neutrino experiment itself shows, however, this is not the case: A tritium film kept over 4 days at 1.7 K did not show any increase of scattered light and therefore not any indication for a film roughening.[10] Moreover, the beta spectrum of a T_2 film prepared and kept at 1.8 K over more than 4 weeks did not exhibit any change of its shape with time. This spectrum can be described consistently by taking the energy loss into account for a homogeneously flat film, in contrast to the spectra of previous measurements with T_2 films kept at about 3 K and briefly even at 4.2 K.[4, 18] This demonstrates the paramount importance of utter experimental control of the source conditions in order to avoid artifacts in these measurements.

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