Influence of the concentration of H_2–D_2 mixtures on their triple-point dewetting behavior

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Triple-point dewetting of pure gases like hydrogen and deuterium on solid substrates is a well-known phenomenon. This property persists even for the mixed system of H_2 and D_2. There exists an effective triple-point temperature $T_3^{(mix)}$, between the T_3 of pure H_2 and the one of pure D_2, which depends on the species concentrations. We present new investigations for a wide range of H_2–D_2 concentrations measured under different thermodynamic conditions. This allows us to map out $T_3^{(mix)}$ as function of concentration, which can be different in the melting or solidifying direction. Furthermore, it turns out that the time the system needs to reach an equilibrium state can be very long and depends on concentration. This is not observed for the pure H_2 and D_2 system. Sometimes the relaxation times are so extremely long that significant hysteresis occurs during ramping the temperature, even if this is done very slowly on a scale of hours. This behavior can be understood on the basis of mixing and demixing processes. Possible differences in the species concentrations in the gas, liquid, and especially solid phase of the system are discussed. A preliminary phase diagram of the H_2–D_2 system is established.

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1. Introduction

Wetting of solid substrates, exposed to a gas in thermodynamic equilibrium, is an ubiquitous phenomenon with both fundamental aspects [1,2] and important applications [3–5]. Microscopically the wetting of a substrate by a liquid film is caused by a strong substrate-particle attraction mediated by van der Waals forces. At present an almost complete microscopic understanding of wetting on a well-defined solid substrate is available [1,2,6]. The main prediction of all these studies, for given thermodynamic parameters such as temperature and pressure, is that the thickness of the liquid film is a function of the substrate-particle and interparticle interactions. In other words, if the van der Waals force between substrate-adsorbate becomes stronger than the interparticle interaction then complete wetting of the substrate, i.e., diverging of the thickness of the liquid layer at the coexistence line is expected. Dewetting will occur if the attraction is weak. In the latter case the growing of the liquid film will become energetically unfavorable and dewetting will take place by forming droplets on a very thin (a few atomic layers) liquid film on the substrate. In the solid phase, however, even in the case of strong substrate-adsorbate interaction dewetting occurs due to the lateral stress induced by substrate roughness [7,8]. This leads to the T_3 dewetting as observed in our systems.

In this work, we have investigated the wetting-dewetting of both pure and binary system of H_2 and D_2 on a gold substrate. Applying D_2 as impurity component in the H_2–D_2 dilute mixture was motivated by both its similar structure to H_2 and its different physical properties from H_2. Moreover, D_2 is a slightly weaker wetting agent in the solid phase than H_2 [9] and has a relatively small zero-point motion (in comparison with H_2 negligible [10]). Therefore the interaction between molecules and substrate atoms is to be different for H_2 and D_2. Regarding substrate roughness our experiments are in a range where the difference between the two isotopes (in their pure form) is negligible. We discuss how the concentration of D_2 modifies the effective triple-point of the two-component system.

2. Experimental procedure

All the experiments presented here were performed by utilizing the surface plasmon spectroscopy, which allows to determine the layer thickness of an adsorbed
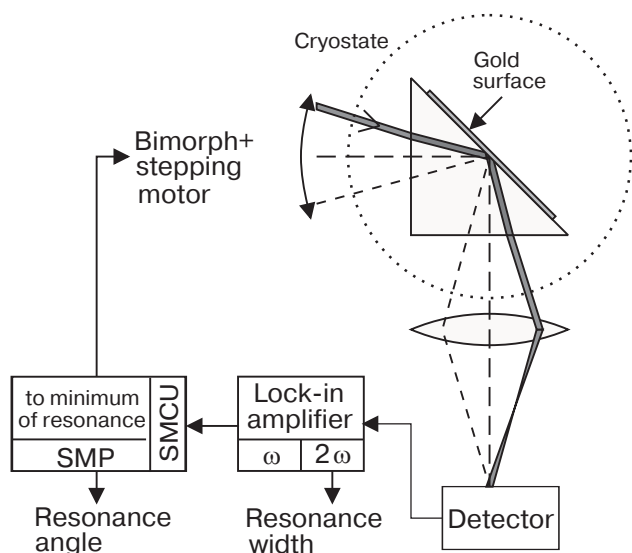
Fig. 1. Experimental setup: Surface plasmon resonance is enhanced at the interface of a gold substrate and an adsorbed medium. The angle of the incident light is modulated by means of a bimorph. Via a lock-in amplifier the intensity signal is coupled back to a stepping motor control unit (SMCU) so that the angle of minimum intensity (i.e. resonance) is kept. From the shift in angle relative to the bare gold surface the thickness of an adsorbed film can be determined.

medium with high resolution (up to a few tenths of a monolayer). The substrate in our measurements was a gold film (45 nm thick) evaporated onto the base of a glass prism. The experimental setup is shown in Fig. 1, more details can be found in Ref. 11. However, the signal processing in comparison to the previous experiments has improved, therefore it resulted in more precise measurements giving results with improved accuracy. The system was fully computer controlled, so, e.g., parameters like temperature could be swept up and down in time very slowly in small steps. This was done several times to check for reproducibility of the measured data. The height and width of the ramping steps, as will be discussed in the results, were chosen, firstly, according to the normal relaxation of the system under investigation and, secondly, to fulfill the equilibrium thermodynamic conditions during the experiment.

3. Results

Presented here are the results of wetting-dewetting measurements of both pure H_2 and D_2 as well as mixtures of both isotopes. As typical examples for the mixed systems we discuss 10 and 50 % D_2 samples. The numbers are molar-percentages of D_2 in the mixture of H_2 and D_2, and the samples were prepared as

follows: after taking an adsorption isotherm of H_2 at 16 K and then raising the temperature to 19 K followed an adsorption isotherm of D_2 in order to reach a certain concentration ratio. Afterwards, ramping the temperature in the range of 10 to 20 K was done. In Fig. 2 the T_3 dewetting of pure H_2 and D_2 and the effective triple-point wetting-dewetting of the mixture of them are plotted. It is observed that for each mixed system the cooling and warming curves reveal a large hysteresis, which is not found for the pure H_2 and D_2 temperature runs. The hysteresis reveals to be solid and stable.

The triple-point temperatures for pure H_2 and D_2 are 13.85 and 18.55 K, respectively. These temperatures, which indicate the onset of dewetting, show within an accuracy of 50 mK no significant hysteresis. For the 10 %-doped system, the dewetting (cooling) and wetting (warming) temperatures are 14.30 and 14.65 K, respectively. For the 50 %-doped system the dewetting and wetting temperatures are 16.75 and 17.30 K, respectively. In order to examine the genuineness of the hysteresis, another 50 % mixture of H_2–D_2 was prepared, but this time at room temperature. Thereafter the adsorption isotherm of the mixture was taken at 20 K. Furthermore three complete cycles, i.e., cooling from 20 K down to 10 K and return with steps of 25 mK/min and a resolved time of 2 min between two successive steps, were done. Figure 3 summarizes the results. A hysteresis of essentially the same width exists even when doing the measurements at lower
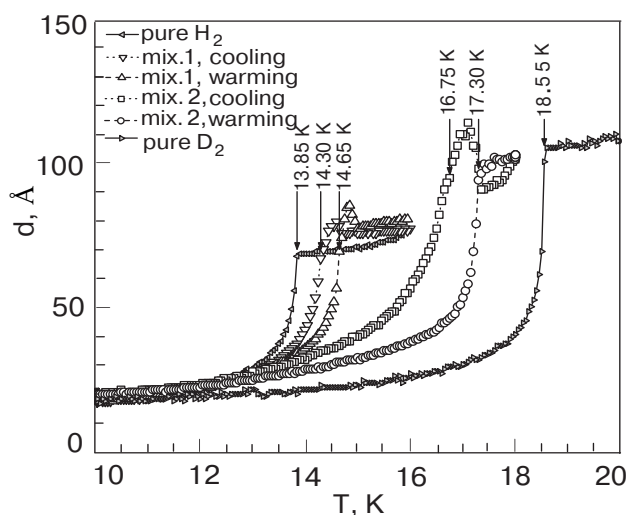

Fig. 2. The dewetting curves (film thickness d against temperature) of pure H_2 ($\triangleleft$), pure D_2 ($\triangleright$), cooling ($\triangledown$) and warming ($\triangle$) of 10 %-doped mixture (mix. 1), and cooling ($\square$) and warming ($\bigcirc$) of 50 %-doped mixture (mix. 2). For pure systems the cooling and warming curves trace the same path. Arrows show the positions together with the values of the wetting transition, i.e., the effective T_3.
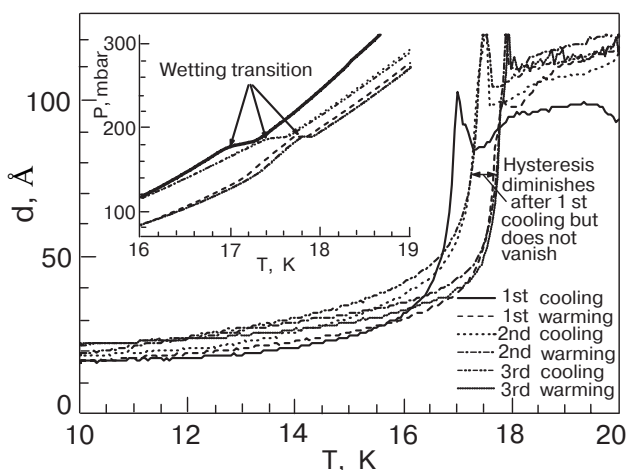
Fig. 3. The dynamics of an equimolar mixture of H_2–D_2 is shown by monitoring the film thickness d over temperature. The temperature scans are done three times. The big hysteresis during the first cooling and warming is attributed to incomplete mixing. The inset shows the associated vapour pressure curves.

ramping speeds, e.g., 10 mK/min. We should mention that during the first scan the hysteresis appeared in a more pronounced way as shown in Fig. 3.

In the inset of Fig. 3 the associated vapour pressure curves are plotted. It shows that the slope of each curve levels off somewhere in the middle of the curve and rises again. The effective triple-points of wetting and dewetting occur exactly at the point of the lower kink for both cooling and warming curves. In order to understand this behavior, in Fig. 4 we have redrawn the supplementary vapour pressure curves of Fig. 2. The solid curves, placed between the vapour pressure curves of pure H_2 and D_2, are calculated pressure curves of the binary systems of H_2–D_2 with different concentrations of D_2 derived from the partial pressure law

$$P_{\text{total}}(T) = C_{D_2}P_{D_2}(T) + (1 - C_{D_2})P_{H_2}(T), \quad (1)$$

where C_{D_2} is the D_2 concentration in the mixture and $P_{D_2}(T)$ and $P_{H_2}(T)$ are the pressure of H_2 and D_2 at given temperature T, respectively. Having obtained these values, one can calculate the total pressure of the mixture under the assumption that the concentration of the species remains constant in the solid, liquid and gas phase. It is known, that even for an ideal binary mixture this condition does not hold, and the data plotted in Fig. 4 illustrate this deviation. The data demonstrate that the concentration of D_2 in the liquid phase increases as the temperature raises and vice versa. Furthermore, the size of the hysteresis and the deviations from the predicted standard curves depend on the concentration of the D_2 phase in the mixture. The size of the hysteresis is largest for con-
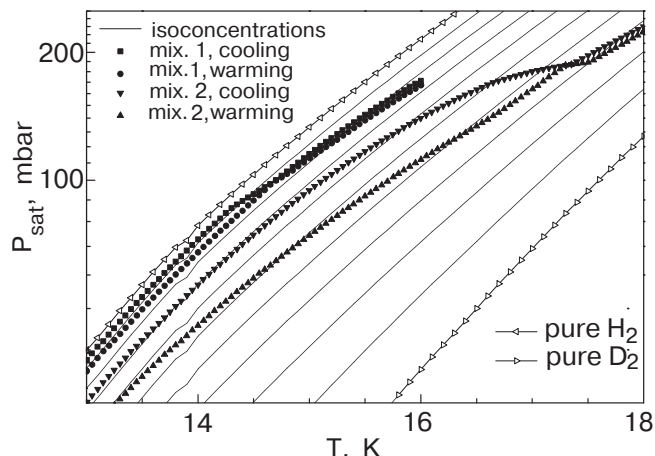

Fig. 4. The corresponding vapour pressure curves of Fig. 2. The solid lines are calculated vapour pressure curves (Eq. (1)) for different concentrations of D_2. Pure H_2 and D_2 pressure curves are also plotted.

centrations around 50 % and diminishes with increasing fraction of either species.

Using Eq. (1), one can extract the D_2 concentration in the liquid phase from the measured vapour pressure curves of the pure H_2, D_2, and the mixture of them. So we have

$$C_{D_2} = \frac{P_{\text{mix}}(T) - P_{H_2}(T)}{P_{D_2}(T) - P_{H_2}(T)}, \quad (2)$$

where $P_{\text{mix}}(T)$ is the vapour pressure of the mixture at a given temperature. Figure 5 displays the evolving of the D_2 concentration in the liquid phase of the two previously introduced sets of mixtures (see Figs. 2 and 4). The solid line, which is extended between the T_3's of the pure H_2 and D_2, is a fit to the transition line obtained from Fig. 6. The small dips in the curves, near 13.85 K, occur precisely at the position of the T_3 of pure H_2. The concentration of D_2 in the liquid phase increases gradually as the temperature rises and vice versa. The noticeable effect is the steep increase (decrease) of D_2 concentration along the transition line during warming (cooling) of the system. In summary, in Fig. 6 the effective triple-points of all the investigations are plotted against the D_2 concentration in the liquid phase. The curve fitted to the data shows that the behavior of the wetting-dewetting temperature against the liquid concentration of D_2 is not linear. (It should be pointed out that the effective T_3 values of both heating and cooling, $T_3^{(\text{up})}$ and $T_3^{(\text{down})}$, lie on this curve.)

The observed behavior can be interpreted by taking into account the temperature dependent differences in concentration in the gaseous, liquid and solid phases inside the sample cell. Let us consider, e.g., a mixture with a nominal D_2 concentration of 50 %: i) When we
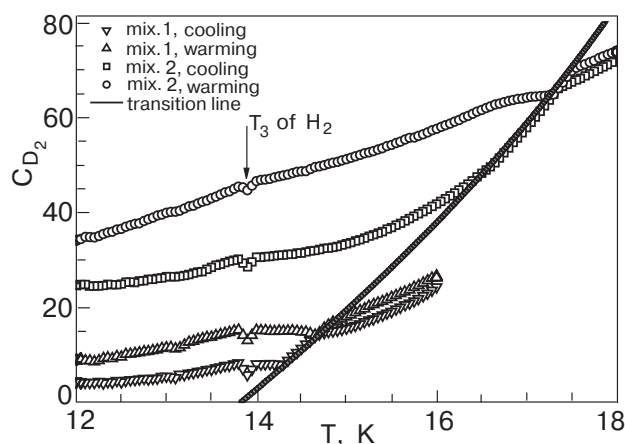
Fig. 5. The rising (falling) of the D_2 concentration in the liquid phase (Eq. (2)) during warming (cooling) for the two mixtures, as presented in Fig. 2. Along the transition line the rising is rather steep, which in turn is the sign of wetting (dewetting) when warming (cooling).

start at *high* temperature at gas-liquid coexistence, a thick liquid wetting film will be present on the substrate, as it is observed in our measurement. As the temperature is lowered and the *liquidus* curve of the mixture is reached (at ≈ 17 K in this case [12]), solid will start to form at the bottom of the sample cell, with a concentration distinctly higher than 50 % (given by the *solidus* curve at that temperature). Upon decreasing T further, the D_2 concentration in the remaining liquid — both at the bottom of the cell, and on the surface where we measure the film thickness — drops, until eventually all bulk liquid has crystallized. At that point ($T_3^{(down)}$) the drop in film thickness, characteristic of T_3 dewetting, starts to take place. ii) For a run starting at *low* temperature,
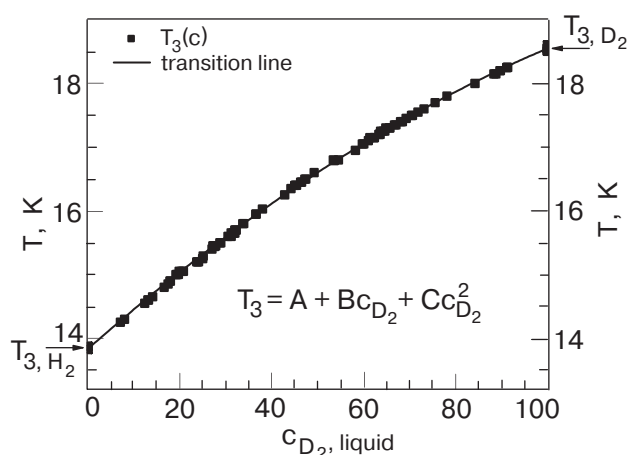

Fig. 6. The experimental data of the effective triple-points of all the investigated mixtures as well as the ones for pure H_2 and D_2. The solid curve is a fit to the data, with $A = 13.83$ (which is the T_3 of H_2), $B = 6.366 \cdot 10^{-2}$, and $C = -1.646 \cdot 10^{-4}$.

on the other hand, the bulk solid has — due to homogenization at $T > 12$ K [12] — a homogeneous concentration of about 50 % throughout the whole sample. Upon increasing T the first bulk liquid will appear in the cell when the solidus curve is met (≈ 15.5 K in this case). However, only at higher temperature the thickness of our film, when in coexistence with bulk liquid of the right concentration, will have reached its «complete wetting value» of about 100 Å, identifying $T_3^{(up)}$. Since $T_3^{(down)}$ and $T_3^{(up)}$ do not coincide, due to the paths in the phase diagram as described, a hysteresis results, as it is in fact observed.

4. Conclusions

In summary we have shown that mixtures of the simple van der Waals adsorbates of hydrogen isotopes are well-suited for investigations of the wetting behavior of binary systems. In pure H_2 and D_2 the adsorbed films display the phenomenon of triple-point wetting (i.e., dewetting sets in rapidly as the temperature is decreased below T_3), and we have studied how this behavior is affected, when instead of a one-component system a mixture of H_2 and D_2 is used (where strictly speaking a triple-point does not exist). It is found that the feature typical for triple-point wetting — the rapid drop in film thickness below T_3 — persists, but the characteristic onset temperature is different for cooling and for heating, in contrast to pure systems. We attribute this hysteretic behavior to the different concentrations of the hydrogen isotopes in the solid, liquid and gas phases, respectively. Our results suggest that the method applied here does not only yield insight into the wetting behavior of mixed systems, but a further analysis of the data should also provide detailed information on the phase diagram of H_2-D_2 mixtures.

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