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Surface melting of deuterium hydride thick films

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Résumé. — Nous avons utilisé la diffusion quasi-élastique de neutrons pour mesurer, en dessous
de la température de fusion, l'épaisseur et le coefficient de diffusion de la couche mobile de
surface de films d'épaisseur 8 et 10 couches moléculaires d'hydrure de deutérium (HD) condensés
sur MgO(100). Les mesures montrent que la surface compacte de HD solide subit une préfusion
avec une épaisseur de la couche fondue variant de 0.5 à 6 couches moléculaires dans le domaine
de températures s'étendant de 4 K à 0.05 K en dessous du point de fusion (16.604 K). Les
coefficients de diffusion tombent dans le domaine des 10^{-5} cm² s⁻¹, ce qui indique que la couche
de surface désordonnée se comporte comme un liquide.

Abstract. — Quasi-elastic neutron scattering has been used to measure, below the bulk melting
temperature, the thickness and the diffusion coefficient of the mobile surface layer of 8 and 10
layer thick films of deuterium hydride (HD) condensed on MgO(100). The measurements show
that the close-packed surface of solid HD surface melts gradually, with the thickness of the melted
layer increasing from 0.5 to 6 molecular layers as the temperature rises from 4 K to 0.05 K below
the bulk melting temperature. The diffusion coefficients are in the 10^{-5} cm² s⁻¹ range indicating
that the surface disordered film is liquid-like.

Strong efforts have been devoted during the last few years to understand surface melting [1-
3], a phenomenon characterized at temperature near but below the melting point
T_m by the existence of a mobile film that wets the solid-vapor interface. From the various
experimental studies carried out so far it seems that the (111) densest faces of fcc crystals have
different behavior for metals like Pb [4], Cu [5], Al [6] and molecular solids like rare gases [7,
8] and CH₄ [9]. The close-packed surfaces of metals do not surface melt whereas the same
surfaces of molecular solids do. This effect may be related to the different type of forces
governing metal [10] and van der Waals interactions [2], but the problem is not settled [11].

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One of the aims of this study is to see whether the densest surface of another molecular solid, hydrogen, undergoes a melting transition.

Condensed molecular hydrogen (H_2) is the substance with the lowest temperature solid-liquid-vapor triple point (T_t). Zero point motion lowers T_t to 13.9 K, well below the classical corresponding states value of about 26 K for an H_2-H_2 interparticle potential with a well depth of 37 K [12]. Adsorption isotherms of films of H_2 physisorbed on MgO smoke, a substrate formed by MgO microcrystals of 800 Å average size and with mostly (100) facets exposed for adsorption, show growth up to at least 7 layers thickness [13]. Above the second layer this growth appears to be in the form of well defined layers at low temperatures, the « n » and « $n + 1$ » layers coexistence regions leading to critical points in the vicinity of 10.3 K. The succession of critical points indicates a roughening temperature in the vicinity of 10.3 K, or about 74 % of T_t, somewhat lower than the 80 % of T_t reported for « classical » rare gases adsorbed on graphite (2,7). Molecular H_2 adsorbed on MgO thus appears to be a good candidate for studying surface melting near T_t, since it either completely wets or is able to form very thick layered films on this substrate, with the possibility that quantum effects extend the range of existence of the surface melted layer due to zero point motion.

Quasi-elastic neutron scattering measurements are well suited to study the temperature dependence of both the thickness and mobility of surface melted layers [9, 14, 15]. Of the various isotopic forms of molecular hydrogen, deuterium hydride (HD) is best suited for quasi-elastic measurements due to a large incoherent scattering cross section and lack of ortho-para conversion. It has the disadvantage that it is less quantum than H_2, with $T_t = 16.604$ K. Adsorption isotherms of HD on MgO performed prior to this experiment indicate identical behavior to that of H_2/MgO, with layering transitions critical points at about 12.4 K [16]. Although no structural information is available for HD/MgO films, the structure of D_2/MgO thick films is partially known [17], the D_2 multilayer film growing in the fcc structure rather that the hcp structure of equilibrium crystals at high temperature (18).

In this paper we present quasi-elastic neutron measurements on « nominal » 8 and 10 layer thick HD films adsorbed on MgO. We are able to demonstrate that the densest plane (111) of HD surface melts, that the mobility of the melted layer is liquid-like and its thickness is a few molecular layers a few tenths of a degree below T_t.

1. Experimental.

The use of uniform powders in surface studies by neutron scattering is useful to increase the surface to bulk ratio because neutrons penetrate easily condensed matter and are usually not sensitive to surfaces. Here we used sintered powders of MgO cubes [13] having a specific area of 13 m^2/cm^3. Their uniformity was tested by measuring a Kr adsorption isotherm at 77.3 K on a test pill of 5.745 g, figure 1. The gas-liquid coexistence step and the liquid-solid coexistence substep (arrow) [19] are clearly visible. The QENS experiment was carried out on about 36 g of sintered MgO. Its total area was about 200 m^2 as measured by a CH_4 adsorption isotherm prior to the experiment. The volume STP of one monolayer of hydrogen was defined as the volume of methane needed for one monolayer times the ratio 0.0882 Å^{-2}/0.0639 Å^{-2} of the densities of hydrogen and methane at monolayer completion.

H_2 has a large incoherent cross section ($\sim$ 140 barns at $\sim$ 1 meV) in its $J = 1$ ortho state [20] which permits self-correlation, i.e. mobility, measurements of moving molecules. Unfortunately some ortho-para conversion occurs at low temperature. Parahydrogen has a poor incoherent cross section ($\sim$ 5 barns). To avoid any change in the total scattering cross-section during the time of the experiment, we used deuterium hydride (HD) which has only one quantum state $J = 0$ and exhibits a reasonable cross-section (60 barn) in our neutron energy range.
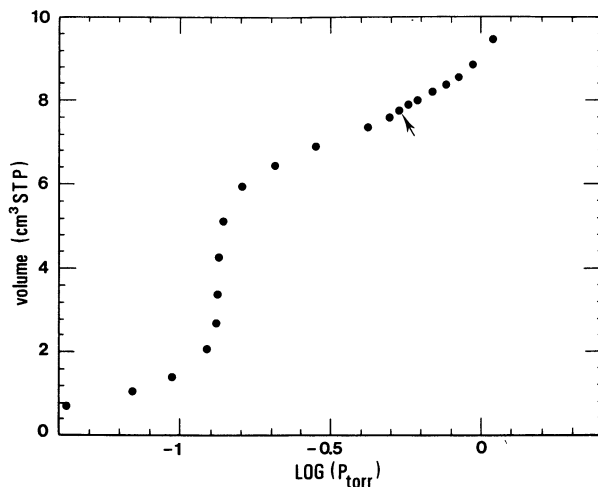
Fig. 1. — Adsorption isotherm of Kr on a sintered MgO(100) powder. The first step corresponds to the two-dimensional (2D) gas-liquid transition in the first adsorbed layer. The substep indicated by an arrow is a signature of the 2D liquid-solid transition.

The MgO sintered pills were processed as indicated in reference [13], baked at 900 °C, transferred in a glove-box into a thin walled stainless steel cell, rebaked at 600 °C and set in the cryostat of the Mibemol instrument at the Laboratoire Léon Brillouin (LLB) in Saclay. The incident wavelength was 8 Å ($E_0 = 1.28$ meV). The instrumental resolution had a triangular shape with a FWHM of 52 μeV. Six detector banks were used at various scattering vectors ranging from 0.35 to 0.95 Å^{-1}. Two sets of experiments have been performed with initial coverages of 8 and 10 layers respectively. The coverages have been corrected for desorption (see table). The multilayer scattering spectra were obtained by subtracting the background due to the cell and to the bare MgO pills. The absolute temperature was obtained by measuring the equilibrium vapor pressure of HD in the cell during the experiment. The uncertainty is better than 0.05 K above 12 K. Two runs have also being performed at the Institute Laue Langevin (ILL) in Grenoble on the IN5 instrument by using the same incident wavelength but with a better resolution (27 μeV). One was a reproducibility experiment with an initial thickness of 10 layers (see Tab. I). The second was devoted to the measurement of liquid bulk mobility (in fact ~ 30 layers) of HD at 17.5 K.

2. Results.

Neutrons can gain or lose energy by interacting with moving molecules. As a result, in a QENS experiment, the fluid part of a sample can be detected by a broad component in the scattering function which is defined as the variation of the scattered intensity *versus* neutron energy at constant scattering vector **Q.** The remaining solid part of the sample yields a narrow resolution limited peak.

Typical recorded spectra are represented in figure 2. They display the variation of the scattering function $S(Q, \omega)$ for three different temperatures below $T_t = 16.604$ K at constant scattering vector $Q = 0.82$ Å^{-1}. The figure reflects the dramatic evolution of the spectra with *T*. At 8.3 K the film is fully solidified whereas at 15.62 K and 16.49 K the observed wings are a clear signature of the existence of a mobile phase. We checked that the integrated intensity remains constant (within a small change due to the Debye Waller factor) for the 3 spectra.

Table I. — *List of the experimental conditions (first two sets of measurements performed at the* LLB, *the last one, at the* ILL) *of the measured thickness of the mobile layer and of the diffusion coefficient D obtained from the two-dimensional and the three-dimensional Brownian model.*

Coverage (layers)	T (K)	x	« liquid » thickness (layers)	D $(10^{-5}$ cm^2 s^{-1} 2D model	3D model
8	8.3	0	0		
8	11.89	0.06	0.5	4	1
7.6	14.455	0.15	1.1	4	1.5
7.1	15.62	0.2	1.4	4.5	2
6.9	15.95	0.3	2.1	4.5	2.2
6.8	16.185	0.4	2.7	5	3
6.7	16.335	0.5	3.35	5	3
6.6	16.405	0.55	3.6	5	3
6.5	16.490	0.6	3.9	5	3
~ 6	17.0	0.7	4.2	5	3
8.8	16.135	0.3	2.6	5	3
8.7	16.300	0.4	3.5	5	3
8.6	16.385	0.5	4.3	5	3
8.5	16.490	0.65	5.5	5	3
8.5	16.520	0.7	6	5	3
8.5	16.545	0.7	6	5	3
9	16.38	0.53	4.8	5	2.9

This means that a part of the solid is transformed into a liquid-like phase whose proportion increases with temperature.

The data reduction method has been explained at length in several papers [9, 15]. We do not want to duplicate the equations here. We just summarize below the hypothesis used in our analysis.

— We assume a solid-liquid stratification (consistent with the layer-by-layer condensation observed in adsorption isotherm measurements). We assign a mean thickness x and an average translational diffusion coefficient D to the mobile part and a remaining mean thickness $(1 - x)$ to the solid part. Hence this « two-phase » system can be characterized by only two adjustable parameters x and D.

— The broad component i.e. the fraction x of mobile phase can be represented either by a three-dimensional (3D) or a two-dimensional (2D) model. The analytical form of the corresponding scattering function is a Lorentzian equation whose width is proportional to DQ^2 at small Q i.e. in the experimental conditions of our QENS recording.

— The contribution to the neutron spectra of the rotational diffusion of the HD molecule is very small as seen by the absence of wings even on a magnified scale for spectra recorded at low T in the solid phase. This means that the rotational diffusion coefficient of HD is very large as known from previous works that show that HD is an almost free rotator [21]. Hence we may neglect the rotational diffusion component except for the well-known form factor $j_0^2(Qr)$ in the scattering law (j_0 is the spherical Bessel function of zero order and
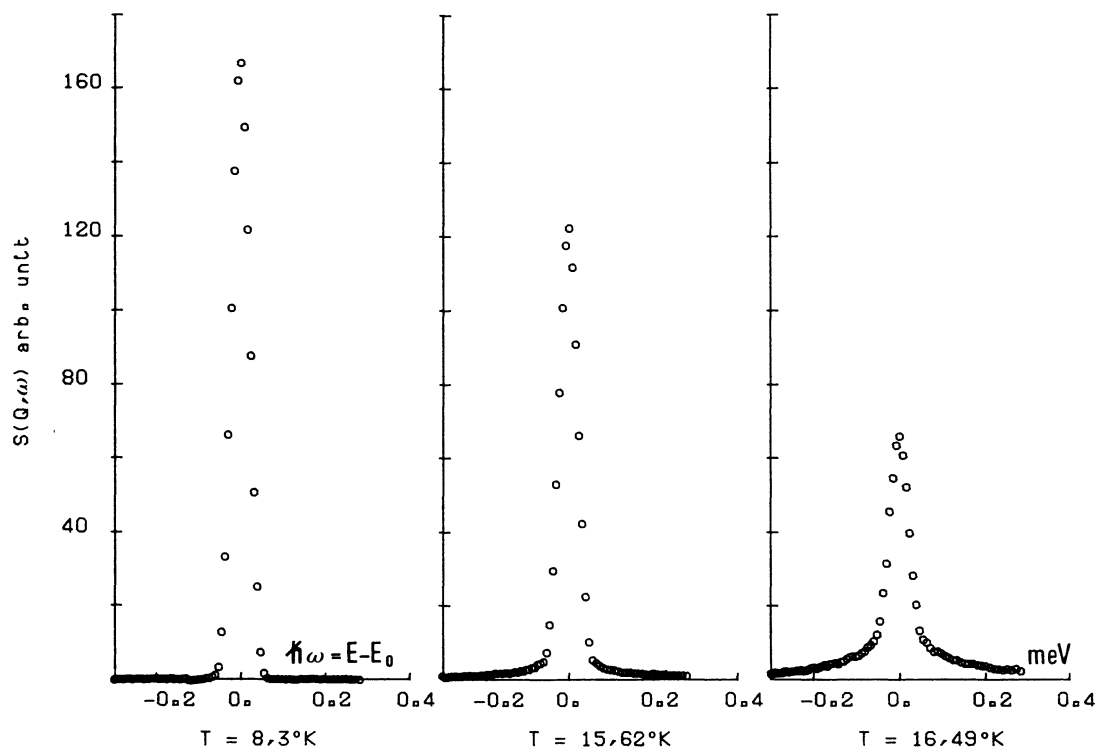
Fig. 2. — Recorded QENS spectra at $Q = 0.82$ Å^{-1} for an initial HD film of 8 molecular layers. The wings displayed at $T = 15.62$ and 16.49 K are a clear signature of the existence of a fluid on the surface at temperatures below $T_m = 16.606$ K. The film is fully solidified at 8.3 K.

$r = 0.37$ Å is the gyration radius of the HD molecule). We also set the Debye-Waller factor to unity.

Hence the coefficient of translational diffusion D and the fraction x of the mobile phase are obtained from the width and from the relative intensity of the broad component of the scattering function respectively. These two adjustable parameters are determined for each physical condition (see table) from the corresponding 6 recorded spectra.

Quasi-elastic neutron scattering functions do not exhibit any wings at 1.85 and 8.3 K. At those temperatures the film is fully solidified. From 11.89 K onward, broad components are observed on the spectra. These spectra are tested against the « two-phase » model where the mobility of the disordered phase is represented either by a 3D or a 2D Brownian motion. The different fits cannot distinguish between the 2 types of motion. This drawback results from the relatively small cross-section of HD. Still our measurements yield the diffusion coefficient and the « liquid » thickness of the surface molten film with fairly good accuracy. Besides the obtained values for x do not depend on the chosen model of motion for all physical conditions.

Some typical fits are represented in figure 3 for a 6.5 layer thick film at 16.49 K with a 3D Brownian model ($x = 0.65$; $D = 3 \times 10^{-5}$ cm^2 s^{-1}). The same detailed analysis has been carried out for all the recorded spectra. The obtained values for the translational diffusion coefficient and the « liquid » thickness are collected in the table I and represented in figures 4 and 5 versus $1/T$ and T respectively.
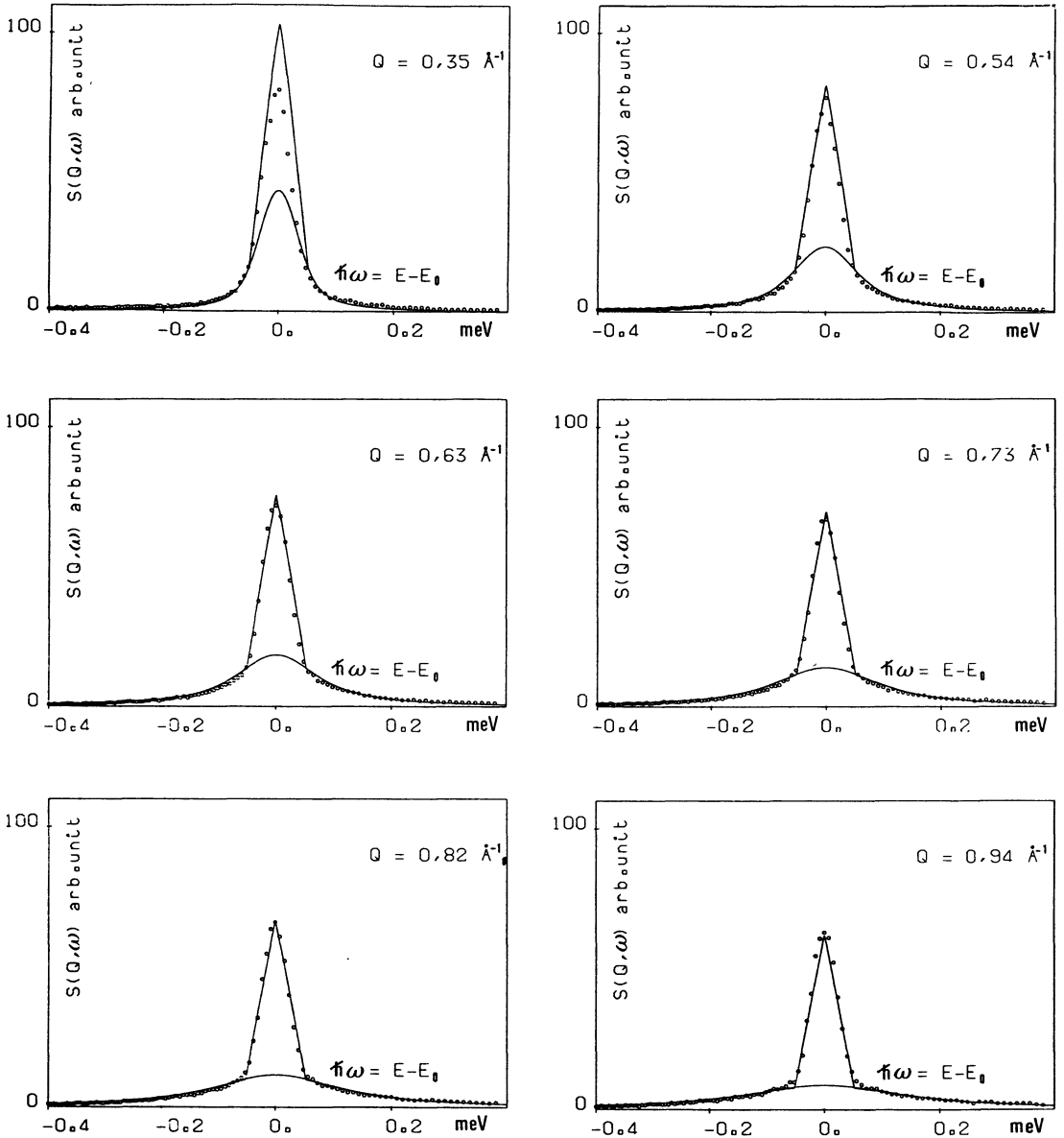
Fig. 3. — Typical fits of the recorded QENS spectra for a 6.5 layer-thick film at 16.49 K width with a 3D brownian model (« liquid » thickness = 3.9 layers ; $D = 3 \times 10^{-5} \, \text{cm}^2 \, \text{s}^{-1}$). The bulk melting temperature for HD is $T_m = 16.606$ K. The Lorentzian component results from the presence of a fluid phase. The narrow resolution limited peak comes from the remaining part of HD solid on the MgO surface.

The measured diffusion coefficients range from 5 to $1 \times 10^{-5} \, \text{cm}^2 \, \text{s}^{-1}$ depending on model and temperature. These values are quite typical for bulk liquid mobility. Hence the molten film is liquid-like. If we consider the data reduction carried out with the 3D Brownian motion model, the diffusivity of the mobile layer obtained just below T_m is equal to bulk liquid diffusivity of HD measured in this experiment ($D = 3.6 \pm 0.6 \times 10^{-5} \, \text{cm}^2 \, \text{s}^{-1}$) (left hand part of Fig. 5). On the other hand the ratio between the diffusion coefficients obtained for 2D and
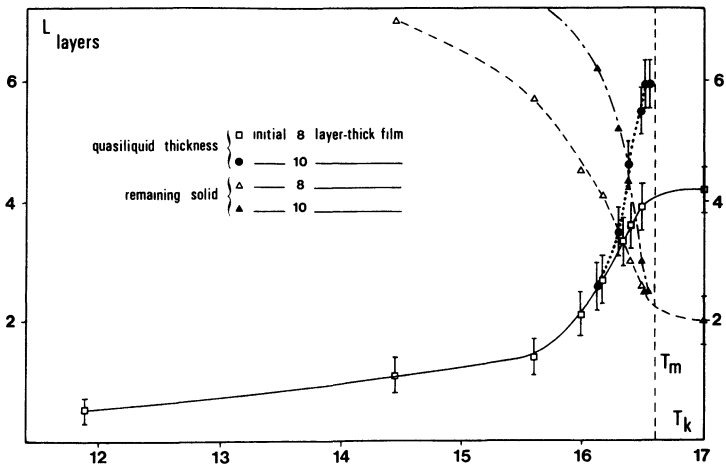
Fig. 4. — Quasiliquid thickness and remaining solid part of the HD film for 2 initial thicknesses (8 and 10 molecular layers). The various lines are guides for the eye.
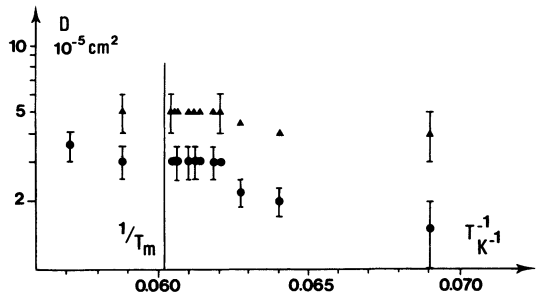

Fig. 5. — Arrhenius plot of the translational diffusion coefficients. On the left-hand side of the figure, the liquid bulk diffusivity measured in this experiment ; on the right-hand side the mean diffusion coefficient of the HD mobile part of the film for a two-dimensional (▲) and for a three-dimensional (●) Brownian model.

3D Brownian motion models is close to 3/2 as expected from theory. Note that the measured diffusion coefficients do not depend on the initial thickness of the film within the experimental uncertainty.

As for the mobile part thickness, the obtained values range from about 0.5 layer at 11.89 K to ~ 6 layers 0.1 K below T_m. These values are comparable, in a reduced temperature scale, to those obtained for surface melting of rare gases [2, 7] and methane (9, 14, 15) (Fig. 6). Figure 4 shows that the molten layer is larger close to T_m for the thickest films (initial 10 layers), an observation indicating that the substrate crystal field tends to solidify the film at the interface HD/MgO. This effect is confirmed above T_m by the measurement at 17 K of a remaining solid film of about 2 molecular layers as shown by the convergence of the solid thickness (dotted lines in Fig. 4) towards 2 layers around T_m. Hence the limited thickness of the initial films and the influence of the substrate as well do not allow us to observe an « infinite » divergence of the molten layer at T_m. Still, the results obtained for a 10 or 8 layer-thick film below 16.35 K are identical. They show that our measurements are representative, below this temperature, of the HD surface melting phenomenon within a good approximation.
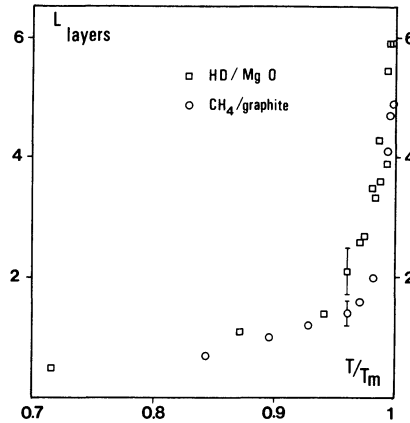
Fig. 6. — Quasiliquid thickness in a reduced temperature scale for the close-packed surfaces of CH_4 (O) and HD (□).

3. Discussion.

Several investigations [1, 2, 7, 22, 23] have been carried out so far so determine the divergence law of the mobile layer thickness at T_m. Results show that the temperature dependence of the « liquid » thickness obeys logarithmic or 1/3 power laws in reduced temperature as it is expected for solids governed by short-range or long-range forces respectively [1-3].

Our measurements could be interpreted in these terms if we do not take into account the results obtained close to T_m because the limited thickness of the whole film imposes a saturation of the number of melted layers at T_m (see Fig. 4). A log-log representation of the liquid thickness *versus* T indicates a power law with exponent 0.6-0.7 which has, as far as we know, no physical meaning for « classical solids ». Still the theory of quantum-mechanical surface is lacking. A semi-log representation shows a somewhat more interesting feature, already visible in figure 4, and deducible from the data of table I. From 11.9 K up to our 15.6 K point the mobile film grows slowly with temperature, with the fitted diffusion coefficient being smaller than the bulk values and slowly increasing in magnitude. We believe that this behavior is due to the « proximity effect », the order of the solid propagating into the liquid at the interface. This has been observed previously for van der Waals systems [7, 24], and in particular for Ne and Ar films adsorbed on graphite, where the ordered liquid thickness is about 6 layers for Ne and 4 layers for Ar. In the HD films we have studied, the thickness of this liquid appears to be at least 2 layers. Above our 15.95 K point the liquid thickness increases more rapidly with temperature and the fitted diffusion coefficient becomes similar to the one of bulk liquid. The finite thickness of the total film though is important here, since desorption has evaporated one layer, and two layers next to the substrate are solid. Saturation of the liquid thickness growth near T_m is evident in figure 4. Given the experimental uncertainly it is not possible to obtain an accurate fit to the growth rate over a very small range of liquid thickness and reduced temperature.

As can be seen from table I and figure 5, the mobility observed at 11.89 K $(T/T_m \approx 0.72)$ involves a thickness smaller than a monolayer (coverage $\sim$ 0.5). From the thermodynamic characterization [16] we know that the roughening temperature for this surface, obtained from extrapolation of the critical temperature of the 2nd, 3rd and 4th layers is estimated to be at 12.4 K. Our observation shows that some mobile molecules are present at the solid-vapor interface below that temperature. This disordering of the surface may be a

precursor state of the roughening transition. It could involve an exchange with the vapor or a motion on the surface due to the appearance and proliferation of vacancies and adatoms which precede the roughening transition [25]. Such a dynamic solid surface-vapor or vacancies stimulated mobility regime has been recently observed below the roughening transition in the case of argon multilayer films adsorbed on graphite [26].

As recalled in the introduction quantum effects in surface melting may be possible in hydrogen films adsorbed at low temperature. Figure 6 represents in a reduced scale the variation of the quasi-liquid thickness for the close-packed surfaces of CH_4 and HD. Although the error bars are large it seems that the mobile CH_4 thickness is systematically smaller than the corresponding thickness of HD. The slight increase of the HD melted layer with respect to CH_4 is probably related to the large quantum volume of the hydrogen molecule. Considerably longer experiments comparing HD films to « classical » films are needed to settle this point.

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