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Evolution of multilayer Ar films on graphite below and above the bulk triple point : a neutron diffraction study

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Résumé. — On étudie par diffraction de neutrons le mode de croissance de films minces d'argon adsorbé sur de la mousse de graphite (foam) dans la gamme de températures 55,5 K-90,5 K. Un film uniforme est formé à 65,5 K lorsque l'épaisseur est inférieure à 4,5 couches. Pour des recouvrements plus grands, des cristallites commencent à se condenser tandis que le film uniforme continue à croître beaucoup plus lentement jusqu'à une épaisseur de 6,4 couches pour un taux de couverture total d'environ 20 couches statistiques. On présente un modèle qui montre que la condensation capillaire se produit dans des pores coniques et des coins. A 80,5 K, on observe une phase de type liquide de 1,5 couche qui est la signature de la fusion de surface. Au-dessus du point de fusion tridimensionnel ($T_m = 83,8$ K), tous les cristallites ont fondu mais un film solide est toujours présent sur la surface de graphite. Son épaisseur varie de 1 à 3-4 couches en fonction du recouvrement et de la température. On donne la température de fusion de ces films solides. Enfin, le film solide uniforme est comprimé latéralement par rapport au plan (111) tridimensionnel avec une relaxation continue lorsque son épaisseur croît.

Abstract. — Neutron diffraction is used to study the growth behavior of thin films of argon adsorbed on graphite foam in the temperature range 55.5 K-90.5 K. It is shown that a uniform film is condensed at 65.5 K for thicknesses below 4.5 layers. For higher coverages, bulk crystallites start to grow into capillaries whereas the uniform film grows much more slowly to reach a thickness of 6.4 layers for a total coverage of about 20 statistical layers. A model is presented showing that the capillary condensation probably occurs in conical pores and open corners. At 80.5 K, a liquid-like phase, 1.5 layer thick, is observed revealing the occurrence of surface melting. Above the bulk melting point ($T_m = 83.8$ K), all the bulk crystallites have melted but a solid film is still present on the graphite surface. Its thickness varies from 1 to 3-4 layers depending on total coverage and temperature. The melting temperatures of these solid films are reported. Finally, the uniform solid film is laterally compressed with respect to bulk (111) planes with a continuous relaxation when its thickness increases.

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1. Introduction.

The adsorption of argon on graphite has been an important experimental system for the development of the understanding of interfacial phenomena. In the multilayer regime Ar has been used in studies of substrate uniformity and stepwise adsorption [1], complete and incomplete wetting, by RHEED [2] and ellipsometry [3, 4], and the evolution from two-dimensional to bulk behavior, by calorimetry [5, 6]. The RHEED measurements, on a single crystal of graphite, indicated uniform growth up to at least 10 layers at 10 to 20 K. The ellipsometric studies on planar artificial graphite (HOPG) are closely consistent, in showing uniform layer growth to 11 ± 1 layer at 64 K [3] and 12 layers at 59 K [4].

The calorimetric study, on compressed exfoliated graphite (foam graphite) was interpreted in terms of uniform growth to at least 20 layers at 62-70 K. However, other studies have raised doubts that Ar can form such thick films in foam graphite. Recent measurements by neutron diffraction indicate the appearance of bulk crystal characteristics at thicknesses greater than four or five statistical layers at 10 K due to capillary condensation [7, 8]. Vapor pressure isotherms in a somewhat different type of exfoliated graphite powder have shown stepwise adsorption up to at least 5 layers at 63 K, and suggest capillary condensation at higher coverages [9]. An alternative and independent explanation for the bulk formation could be incomplete wetting, and such a claim was made on the basis of measurements on graphite fiber, which gave a maximum thickness of 3-4 layers at 61 K [10]. However, an alternative explanation attributes this sharply reduced limiting thickness to substrate heterogeneity [11]. In addition, it is important to note that detailed calculations of the wetting behavior of physisorbed films on an ideal planar graphite substrate predicts that more than 20 layers of Ar will be stable at low temperature [12]. A more detailed summary of these results is given in an excellent review [13].

In this paper we describe a neutron scattering study of Ar/foam graphite that substantiates the earlier diffraction results and extends the study to a detailed examination of crystallite growth.

2. Experimental details.

The experiment has been performed at the Institute Laue-Langevin (Grenoble, France) on the D20 diffractometer at $\lambda = 2.406 \text{ \AA}$. The substrate was 2.7 grams of graphite foam [14]. It has an adsorption uniformity considerably better than Papyex and Grafoil, according to various techniques of surface characterization [15]. Before the experiment the graphite substrate was baked at 1 000 °C under vacuum (10^{-6} torr) for 12 hours, then transferred into an aluminum cell under helium atmosphere. ^{36}Ar isotope has been used in order to have appreciable coherent elastic scattering. As usual, all the experimental diffraction patterns reported here have had the substrate-sample cell background subtracted. The Q -ranges of interest for the argon diffraction peaks are $1.9\text{-}2.6 \text{ \AA}^{-1}$ and $3.0\text{-}3.5 \text{ \AA}^{-1}$.

A nitrogen calibration isotherm was measured at 77.3 K. It indicated an adsorption area of $26.5 \text{ m}^2/\text{g}$. An argon adsorption isotherm has also been measured in the monolayer range. It allows us to define a coverage of one monolayer equal to $20.8 \text{ cm}^3 \text{ STP}$. For coverages higher than 1 monolayer, the condensation was carried out at 65 K where the equilibrium pressure is approximately 30 mbar. We have studied thicknesses ranging from 2 to 23 layers, and a range of temperatures from 65 K to above the bulk triple point, $T_m = 83.8 \text{ K}$.

The temperature regulation was $\pm 0.01 \text{ K}$ within the temperature range studied which is 55.5 K-90.5 K. The absolute temperature scale is calibrated against the triple point temperature with an estimated accuracy $\pm 0.2 \text{ K}$.

3. Results.

We report here mainly the results obtained at 65.5 K, 80.5 K and above the triple point. The analysis of the diffraction lines is based on the identification of peaks from the 2D hexagonal structure of the uniform solid film and from the FCC structure of bulk argon.

3.1 CHARACTERIZATION OF THE ARGON FILM AT LOW TEMPERATURE ($T = 65.5$ K). —

Figure 1 shows some typical diffraction spectra at $T = 65.5$ K when the total thickness of the argon film is increased. We observe essentially 3 peaks :

- * $Q = 2 \text{ \AA}^{-1}$, it corresponds to the superimposition of the 2D 10 and 3D 111 peaks which have very close Q s.

- * $Q = 2.3 \text{ \AA}^{-1}$, this peak appears when the film thickness increases. It corresponds to a modification of the tail of the 2D 10 peak when the uniform film thickness is larger than 4 layers and also to the 3D 200 peak.

- * $Q = 3.3 \text{ \AA}^{-1}$, corresponding to the 2D 11 and 3D 220 peaks which fall at the same Q position when the layers in the uniform film have the same hexagonal packing as in the 3D (111) plane of bulk.

In order to fit the spectra above 4 layers, we have to combine spectra from a uniform flat film together with that from 3D crystallites. The coverages are therefore measured in equivalent statistical layers (SL), taking into account the uniform film and the crystallites. We know from previous studies [7, 16] that the film grows with a hexagonal packing parallel to the surface, similar to the (111) bulk plane. Then stacking faults may occur, but it is difficult to predict the actual stacking sequence for thin films, even though the ABC sequence (FCC structure) is the most stable for bulk argon [17]. Strong modifications of the diffraction lineshape result from these faults as shown by Larese *et al.* [7]. Considering every possible

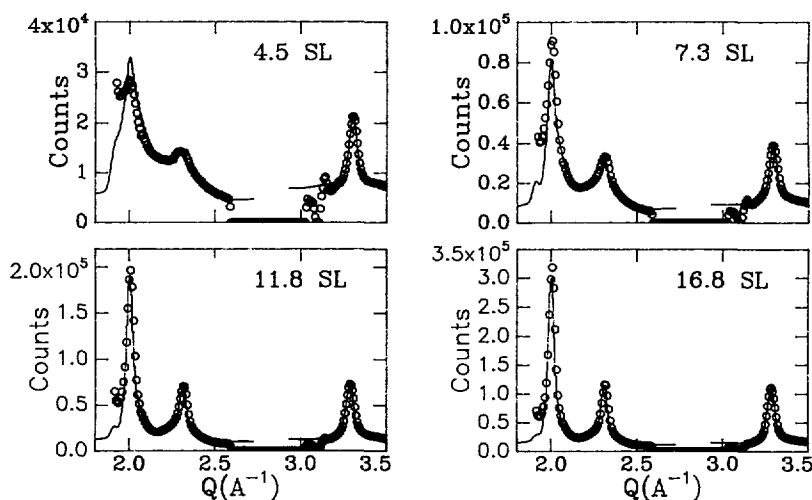


Fig. 1. — Diffraction patterns of Argon films adsorbed on graphite at 65.5 K. a) 4.5 statistical layers (SL), b) 7.3 SL, c) 11.8 SL and d) 16.8 SL. The 2D (10) and 3D (111) peaks are found around 2.0 \AA^{-1} ; the 2D (11) and 3D (220) peaks are around 3.3 \AA^{-1} . The peak at 2.3 \AA^{-1} is the 3D (200) peak appearing with increasing coverages. The calculated lines (solid lines) are fitted against the experimental data (open circles). The calculated patterns result from the superimposition of a crystallite pattern and of a uniform film pattern. The parameters are given in table I.

packing sequence for a given thickness, the most substantial differences appear in peak positions between the ABCABC... (FCC-like) and ABAB... (HCP-like) sequences and are located around 2 \AA^{-1} . In the work reported here, we have limited ourselves to these two packing sequences, since a detailed analysis of the stacking faults was not our purpose. The experimental spectra cannot be fitted using a single ABC stacking sequence for the uniform solid film and we have assumed a combination of the FCC-like and HCP-like sequences. The adjustable fit parameters are :

- a scale factor which is the same for all measured spectra ;
- the thickness of the uniform solid film ;
- the proportion FCC/HCP in the uniform film ;
- the amount of bulk crystallites ;
- the parameter of the uniform film.

Some typical fits are shown in figure 1 and the parameters used for the calculated lines are reported in table I. Special care was taken for the fitting of the peak at $\sim 3.3 \text{ \AA}^{-1}$ that is used to calibrate the total amount of solid. When the coverage of the Ar film is increased from 4.5 to 17 SL, the thickness of the uniform film increases gradually whereas the amount of 3D crystallites increases much more rapidly. For 4.5 SL, there is almost no crystallites. At 65.5 K, the Ar film, thicker than 4 layers, is completely solid. The lattice constant is measured at 65.5 K for the 3D crystallites $a = 5.420 \pm 0.005 \text{ \AA}$ and it is in close agreement with the literature [18]. The size of the crystallites is at least equal to the coherence length of the neutron beam ($\sim 300 \text{ \AA}$). The uniform solid film is very weakly compressed ($\sim 0.6 \%$) with respect to the (111) 3D plane. The best fits are obtained after introducing 20 % (thin films) to 10 % (thicker films) of stacking faults of HCP type in the packing of the film. It is worth noting that the uniform film continuously relaxes as it becomes thicker. The lattice constant increases from 5.371 \AA , for the bilayer to 5.390 \AA , for a 6-layer uniform thick film at 65.5 K. Within the thickness range investigated in this study, the uniform solid film is always compressed with respect to the (111) bulk plane.

Table I. — *Parameters of the calculated diffraction lines shown in figure 1, for different films of argon adsorbed on graphite at 65.5 K. The accuracy of these parameters is 0.2 monolayer, 0.005 \AA and 5 % for the thicknesses, the lattice constant and the proportion of FCC or HCP stacking sequence, respectively.*

Coverage (*) (statistical) (layer)	Uniform film				Crystallites thickness (**) (stat. layer)
	thickness (**) (monolayer)	Packing		Lattice const. (\AA)	
		% FCC	% HCP		
4.5	4.0	80	20	5.38	0.33
7.3	5.6	80	20	5.39	1.7
11.8	6.0	90	10	5.39	6.0
13.9	6.2	90	10	5.39	8.0
16.8	6.4	90	10	5.39	10.8

(*) Coverage calculated from the quantity of Ar atoms introduced in the cell.

(**) Statistical thicknesses deduced from the fit of the diffraction patterns.

3.2 SURFACE MELTING OF THE ARGON FILM. — The diffraction pattern of the solid bilayer was measured at 55.5 K and 65.5 K. An estimate of the thermal expansivity of the bilayer at 60 K is deduced from this measurement : $3.3 \cdot 10^{-4} \text{ K}^{-1}$. A dramatic change in the intensity of

the peak around 3.3 \AA^{-1} is observed between 65.5 K and 70.5 K (Fig. 2). We interpret this effect as the melting of the upper layer of the bilayer. This result concerning the melting of the Ar bilayer is in agreement with the measurements of Larese *et al.* [8]. We also measure that the solid monolayer at 70.5 K (which is coated by a liquid monolayer) is 0.3 % compressed with respect to the solid bilayer at 65.5 K.

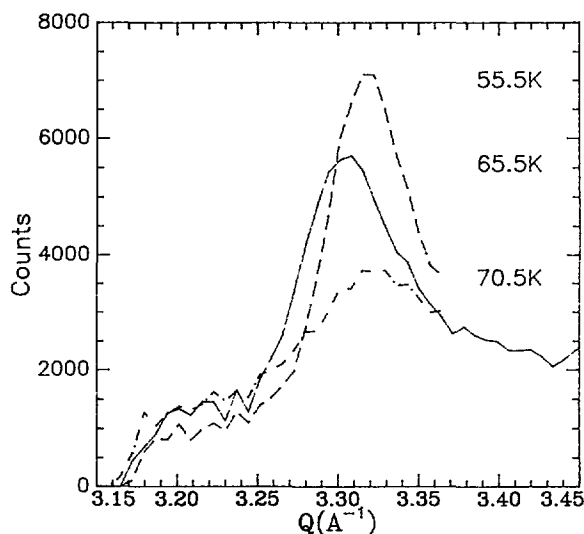


Fig. 2. — Temperature dependence of the diffraction peak at 3.3 \AA^{-1} from a bilayer. The thicknesses and temperatures are 2.2, 2.0, 1.8 monolayers and 55.5 K, 65.5 K and 70.5 K respectively. The peak shifts toward the low Q s between 55.5 K and 65.5 K, due to thermal expansion. It decreases strongly between 65.5 K and 70.5 K, that indicates the melting of the upper layer; the remaining solid monolayer is compressed with respect to the solid bilayer.

Films of different coverages are measured at 80.5 K ($T_m = 83.8 \text{ K}$). The integrated intensity of the (220) peak at $\sim 3.3 \text{ \AA}^{-1}$ is used to determine the total amount of solid, assuming i) that the intensity $I_{220}(n)$ is proportional to the statistical thickness n ; this assumption valid for thick films does not hold for reduced thicknesses-theoretical calculations of diffraction lines show that the ratio $I_{220}(n)/n$ almost constant for $n > 4$, significantly decreases from $n = 4$ to 1-, and ii) that the proportionality coefficient is constant over the full range of temperatures we have investigated. The statistical layer thicknesses of the solid phases (uniform solid film + crystallites) are reported in table II. The differences give directly the thickness of the disordered or liquidlike phase. A more detailed analysis is carried out in order to separate the signatures of the uniform solid film and of the crystallites. A uniform solid film, even 5 layer-thick, only gives a broad bump at $\sim 2.3 \text{ \AA}^{-1}$; the sharp shape of the peak located around 2.3 \AA^{-1} is due to the crystallites (200 peak). We can estimate that there are 1.5 ± 0.5 statistical layers of solid crystallites for a total coverage of 7 SL at 80.5 K, that is almost the same amount as at 65.5 K (Tab. I). This means that the liquid phase, 1.8 layer thick, observed at 80.5 K is completely, or nearly completely due to surface melting of the uniform film. The reason why the liquid arises primarily from the film rather than from the crystallites is that the surface area of the film is much greater. The same analysis is done for the 8.8 SL thick film at 80.5 K revealing that the quantity of liquid is primarily on the uniform

Table II. — Argon films adsorbed on graphite at 80.5 K. The coverage is calculated from the quantity of argon atoms introduced in the cell. The thickness of the solid part (uniform film + crystallites) is determined from the integrated intensity of the diffraction peak at 3.3 \AA^{-1} . The thickness of the liquid part is deduced from the difference of the two other thicknesses. The accuracy of this determination is ± 0.5 monolayer.

Total coverage	Solid thickness (in statistical layer)	Liquid thickness
5.0	3.6	1.4
7.0	5.2	1.8
8.8	7.3	1.5
10.5	9.7	0.8
10.8	9.1	1.7
13.8	11.3	2.5
22.9	17.2	5.7

film. The thickness of the liquid layer at 80.5 K can be estimated to 1.5 ± 0.5 SL as long as the total coverage is smaller than ~ 11 SL. For thicker films, we obtain some increase in the liquid layer thicknesses. The amount of material in the crystallites dramatically increases with the coverage, as shown at 65.5 K, in table I, whereas the uniform film does not grow much more. Assuming that the proportion of crystallites *versus* uniform film remains unchanged between 65.5 K (Tab. I) and 80.5 K, it appears unlikely that the increase in the liquid thickness observed for coverages larger than ~ 11 SL could be ascribed to the melting of the uniform film only, since its thickness does not exceed ~ 6.5 layers. It is reasonable to think that an appreciate amount of liquid comes from the melting of the crystallites grown in the capillaries. We remind that the thickness of the liquid expressed in statistical layers is determined from the total number of molecules in the « disordered » phase and assuming a constant adsorption area. The presence of crystallites modifies the solid-vapor interface area in an unknown way as far as a detailed description of the crystallite shape and number is lacking.

3.3 THE ARGON FILM ABOVE THE TRIPLE POINT. — The experiment has been extended to temperatures higher than the melting point ($T_m = 83.8 \text{ K}$). The diffraction lines are reported in figure 3 for various temperatures ranging from 82.5 K to 84.5 K, and for a constant nominal thickness of 14.9 layers. The sharp peak around 2.3 \AA^{-1} , due to the crystallites disappears suddenly around $T = 83.7 \text{ K}$, that is close to the bulk melting point. Simultaneously, the peak around 3.3 \AA^{-1} decreases considerably when $T \rightarrow 83.7 \text{ K}$ and the remaining peak is shifted toward higher Q s. These observations clearly show that all the crystallites have melted when the bulk melting point is crossed and that a solid film is still present on the substrate surface. Looking at the peak around 3.3 \AA^{-1} , we can characterize more precisely the solid layer above T_m for different coverages. The thermal desorption is, of course, very important in this temperature range and has been taken into account for determining the total coverage. Moreover, for small solid thicknesses, the integrated intensity of the (11) peak is no longer proportional to the coverage.

The characteristics of the (11) peak ($\sim 3.3 \text{ \AA}^{-1}$) are reported in table III for various coverages and $T = 85.0 \text{ K}$. Three classes may be distinguished depending on the total coverage : (i) for a total coverage of 2.2 layers, we observe one solid monolayer ; (ii) for 3.5 and 4.9 layers, the solid film is 2 layer-thick and is 0.5 % expanded with respect to the solid

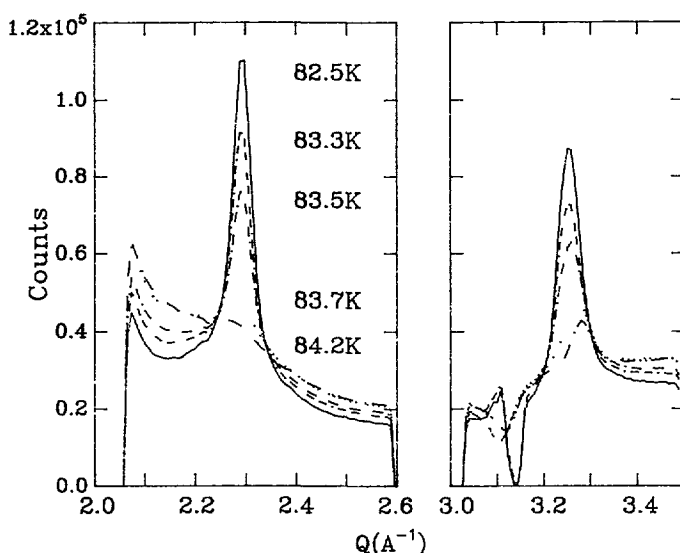


Fig. 3. — Diffraction patterns of a 14.9 statistical layer thick film of argon from 82.5 K to 84.2 K. A strong change in the intensities and peak positions (around 3.3 \AA^{-1}) is observed over 0.2 K between 83.5 K and 83.7 K.

Table III. — Argon films adsorbed on graphite at 85.0 K. Evolution of the (11) peak with the total statistical thickness of the film. The variations of the peak position and width and of the integrated intensity are representative of the thickening of the uniform solid film from the monolayer to 3-4 layers.

Coverage in statist. layer	Peak position \AA^{-1}	Peak width \AA^{-1}	Intensity arb. units
2.2	3.317	0.043	82
3.5	3.302	0.036	250
4.9	3.302	0.032	328
6.0	3.293	0.029	425
8.0	3.291	0.029	448
11.0	3.289	0.028	475
20.0	3.285	0.027	533

monolayer of case (i) ; (iii) for coverages higher than 5 layers, a solid 3-to-4 layer thick film is likely to be present and appears to be $\sim 0.4 \%$ expanded with respect to the previous case. A continuous expansion of the average lattice constant, that can be seen as the signature of the decreasing field of the substrate, is observed when the uniform solid layer thickens from the monolayer to the trilayer. The thickening of the uniform solid film occurs when the total coverage (solid + liquid) is increased, as shown in table III. One might expect that the « weight » of the higher layers would result in a densification of the underlying solid film [6], that is not observed. If this latter effect actually exists, it should compete with the opposite effect of relaxation due to the weakening of the substrate interaction.

When the temperature is further increased ($T \rightarrow 90.5$ K), the melting of the outermost layer of the solid trilayer observed at 85.0 K is clearly evidenced by a discontinuity in the (11) peak position, corresponding to a compression of the solid bilayer with respect to the solid trilayer, and simultaneously the intensity of the peak decreases. A rough estimate of this melting transition can be deduced: $\sim 88.0 \pm 0.5$ K for the thickest films (coverage > 14 layers) and $\sim 86.0 \pm 0.5$ K for thinner films (5-8 layers), see figure 4.

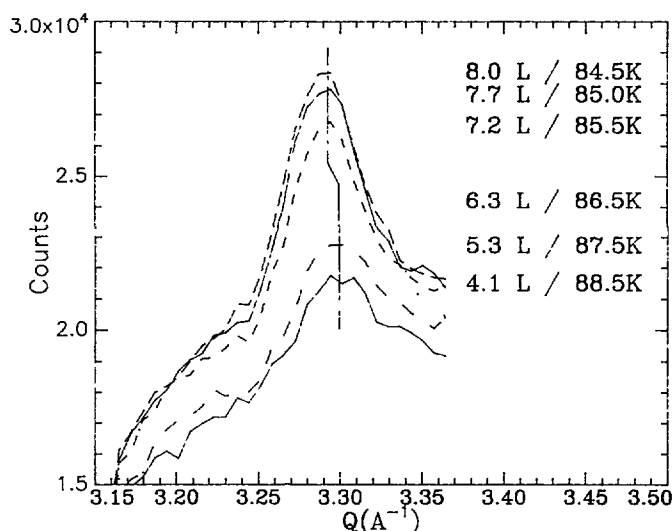


Fig. 4. — Temperature dependence of the diffraction peak at 3.3 \AA^{-1} . The thicknesses and the temperatures are 8.0, 7.7, 7.2, 6.3, 5.3, 4.1 statistical layers and 84.5 K, 85.0 K, 85.5 K, 86.5 K, 87.5 K and 88.5 K respectively. A clear discontinuity is observed between 85.5 K and 86.5 K interpreted as the melting of the upper layer of the solid trilayer still present at $T < 85.5$ K. The solid bilayer above 86.5 K is compressed with respect to the trilayer.

4. Discussion.

The aim of the study reported here is to characterize argon films adsorbed on graphite for different thicknesses to 23 statistical layers and temperatures ranging around the bulk triple point temperature. A description of these films is given in terms of different components: uniform solid film, crystallites and disordered (liquid) film. Our results have to be compared with the earlier neutron diffraction study by Larese *et al.* [7, 8] on thinner films (< 4 layers).

We have measured the lattice constant of the uniform solid film at different coverages ranging from 2 to 6 layers, at 65 K. The uniform solid film is laterally compressed with respect to the 3D (111) plane. A continuous relaxation of the uniform film is however observed when its thickness increases. The same effect of compression of the uniform solid film with respect to bulk is also observed when the film is coated with a liquid layer, as shown in figure 3. The lattice constant of uniform solid films was previously measured by Larese [7] at 10 K. The uniform film was found expanded with respect to bulk with a continuous compression toward the bulk lattice constant when the thickness was increased from 2 to 4 layers. The two measurements are not actually in conflict, since they are at different temperatures. The difference can be ascribed to the distinction between the thermal expansivities of the film and

bulk solid. At 60 K, they are $3.3 \cdot 10^{-4} \text{ K}^{-1}$ (this work, Sect. 3.2) and $4.8 \cdot 10^{-4} \text{ K}^{-1}$ [19], for the uniform bilayer and bulk respectively. This difference in the thermal expansivities explains that the uniform film, expanded at low temperatures, can become compressed with respect to bulk at higher temperatures.

We analyze the intensity decrease of the diffraction peak around 3.3 \AA^{-1} when the temperature is raised, as the signature of the order-disorder transition associated to surface melting. Another possible explanation of the attenuation of the diffraction peak can be put forward: the roughening of the film surface. Roughening is usually represented without change of the lattice parameter of the crystal. Here, the lattice parameter of the film is reduced, when the peak intensity decreases with increasing temperature. In fact, we cannot rule out a certain roughness of the solid-quasiliquid interface making the peak intensity somewhat weaker. This type of roughness, or crystallinity profile was studied for surface melting of methane (100) planes adsorbed on MgO [20]. For this latter system, the 2D (10) peak, the most sensitive to the crystallinity profile was clearly distinct from any substrate peak, making the analysis rather easy. For the present Ar/graphite system, the uncertainty is too large for this kind of determination due to reliable data missing around 1.8 \AA^{-1} (perturbation from the close graphite peak). However, it is worth recalling that roughening is a phenomenon which is likely to compete with surface melting in the explored temperature range.

In agreement with Larese *et al.* study, we also show that substantial bulk crystallization begins at coverages between four or five layers, at temperatures well below the melting point. One of the remarkable features in our data is the very slow growth of the uniform film and the linear increase in the intensity of the bulk peaks. Such behavior would seem to suggest incomplete wetting, although in the ideal case of a uniform flat substrate the film thickness would be strictly constant after the start of bulk condensation. The experimental trend is also consistent with capillary condensation theory predicting a relatively rapid changeover from film to bulk growth when capillary condensation begins [21, 22]. Here we can show a simple model of such behavior and derive a quantitative criterion for the onset of capillary condensation as a function of pore size, and the dependence of film thickness on total coverage as a function of pore geometry.

We consider a multilayer film attracted to a substrate by long range van der Waals forces. At moderate thickness, where retardation is not important, the pressure-thickness relation is

$$P = P_0 \exp(-\alpha/kTt^3) \quad (1)$$

where P_0 is the saturated vapor pressure, t is the thickness and α is the substrate interaction parameter. Equation (1) describes complete wetting on a planar substrate, where P approaches P_0 asymptotically as $t \rightarrow \infty$. However, in small pores the pressure of the saturated liquid falls below P_0 because of capillarity. The decrease is proportional to the film-vapor surface tension and inversely proportional to the radii of curvature r_1 and r_2 of the meniscus: for the case of low density vapor,

$$\delta P/P_0 = - (2 \gamma/\rho r' kT) \quad (2)$$

where ρ is the density of the condensed phase and $2/r' = (1/r_1 + 1/r_2)$ [23]. If the substrate contains both flat regions and capillaries an adsorbate at intermediate coverages can consist of uniform thickness film coexisting with bulk material in the pores. The thickness of uniform film equilibrium with the capillary condensed material is found by equating equations (1) and (2):

$$\delta P/P_0 = - 2 \gamma/\rho kTr' = [\exp(-\alpha/kTt^3) - 1] = -\alpha/kTt^3 \quad (3)$$

if $\delta P/P_0 \ll 1$. Thus the thickness varies as the $1/3$ power of the mean meniscus dimension r' :

$$t = (\alpha \rho r' / 2 \gamma)^{1/3} \quad (4)$$

The dependence of thickness on the total quantity of adsorbate is still weaker. In « open » pores and capillaries, where the cross section increases as the pore becomes filled, the volume V_c of adsorbate in the capillary is proportional to the area of meniscus, $\sim r_1 r_2$. To relate the growth of thickness to V_c we consider two specific geometries: conical pores and inside corner regions, where the two radii are approximately equal, and wedges, where one radius is much greater than the other. These two limiting cases give power law relations but with markedly different exponents:

$$\begin{aligned} \text{Conical pores and open corners : } t &= \text{const. } (V_c)^{1/6} \\ \text{Parallel-sided wedges : } t &= \text{const. } (V_c)^{1/3} \end{aligned} \quad (5)$$

Before the start of capillary condensation the thickness grows linearly with dosage; after condensation begins the film grows much more slowly, with an exponent that reflects the geometry of the pores. In any case the growth of thickness with total dosage slows down so greatly that the changeover, as Ball and Evans [21] describe it, has nearly the character of a first order transition. The changeover can also make it appear that the appearance of bulk phase is due to incomplete wetting. Incomplete wetting on a uniform planar interface would show up by P reaching P_0 at finite t and remaining equal as dosage is increased beyond that point. Incomplete wetting on a porous substrate is more complicated, since capillary condensation can hasten the appearance of the bulk phase, so that it begins at a pressure lower than P_0 . But a clear distinction is that in incomplete wetting the thickness of the uniform film will not grow at all beyond its critical value.

We find the experimental results in agreement with the model behavior of capillary condensation. The thickness of uniform film, as measured directly by the intensity of the film peaks, grows very slowly from four to six layers as the number of statistical layers is increased by a factor of four. This behavior is listed in table I and shown graphically in figure 5. We see that the data between coverages of 7.3 and 16.8 SL are described quite well by the power law equation (5) with exponent $1/6$; hence the capillary condensation appears to be primarily into corner regions.

It is expected that capillary condensation will begin in the smallest crevices, with characteristic dimensions much smaller than the mean pore size in a powder. As illustration, we calculate the characteristics in a film of Ar on graphite, assuming capillary condensation starts at a thickness of 5 layers at 65 K. With the adsorption parameter $\alpha/k \approx 1\,200\text{ K} \cdot (\text{layers})^3$, the calculated pressure shift $\delta P/P_0 \approx 0.14$. This ratio, with the value $\gamma \approx 13\text{ erg/cm}^2$ [24] corresponds to a pore radius $r \approx 35\text{ \AA}$. This is much smaller than the average pore radius in foam, which according to its mass and specific adsorption area is about $2 \times 10^4\text{ \AA}$ [25]. However, the condensation must begin in the smallest crevices and corners, for which the characteristic dimensions must be smaller than the pore diameter.

The model provides a quantitative explanation of the present data and the previous neutron scattering results [7]. It also explains some features of the calorimetric data, specifically why the rising portions of the melting heat capacity peaks of different thickness films, for coverages $> 5\text{ SL}$, are virtually identical (Fig. 1 of Ref. [5]). This had been attributed to the absence of an appreciable influence of the substrate for thicknesses greater than about five layers, assumed to be due to a rapid fall off of the field with distance. We can now conclude that the identical shape came about because the signals were due to the surface melting of the uniform film as well as of bulk crystallites. For the highest coverages, the crystallites are

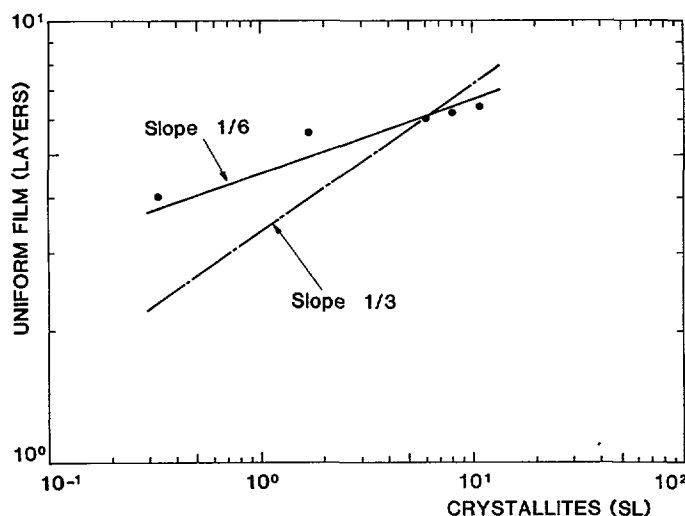


Fig. 5. — Thickness of the uniform film *versus* statistical thickness of crystallites, at $T = 65.5$ K (see Tab. I).

numerous and large and surface melting can therefore progress further before the crystallites completely melt. At lower coverages, no or few crystallites are present and surface melting is rapidly truncated, giving rise to a heat capacity peak with a maximum at lower temperatures. Capillary condensation also explains features of the overall phase diagram, shown as figure 2 of reference [6].

These results from experiments on powdered samples are also in accord with the RHEED study of wetting on graphite single crystals, which found layer growth up to at least 10 layers at low temperature [2], and with the ellipsometry study on a large planar HOPG graphite surface, which observed a limit of 14 layers at 65 K [13]. This limit may be due to intrinsic incomplete wetting; a calculation of the wetting behavior on an ideal graphite surface at 0 K found the film thickness exceeds 20 layers [12]. The maximum thickness on a real surface may be lower than the ideal value, due to substrate imperfections, which cause the film to nucleate polycrystalline multilayers, thereby raising the chemical potential by the grain boundary energy [11].

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