

## Growth of $^4\text{He}$ films on graphite, krypton-plated graphite, magnesium oxide, and Mylar substrates

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Adsorption isotherms of  $^4\text{He}$  on graphite foam, uncompressed exfoliated graphite, krypton-plated graphite foam, MgO, and Mylar indicate type-II growth, i.e., uniform layer deposition up to a critical thickness, and bulk condensation thereafter. On graphite the critical thickness is about four atomic layers; plating with one monolayer of krypton reduces the critical thickness by more than one layer. The critical thickness on MgO is 1.5 layers, and on Mylar is between three and four layers. None of the vapor pressure isotherms obey the exponential  $d^{-3}$  Frenkel-Halsey-Hill equation within the range of the experiments.

### I. INTRODUCTION

Thin adsorbed films of helium have been studied for many years, and have recently come under increased attention.<sup>1</sup> New theories offer the possibility that, contrary to older ideas, superfluidity may occur in films as thin as one atomic layer,<sup>2,3</sup> and some recent experiments<sup>4,5</sup> have been interpreted as confirming the theory. However, the interpretations have been questioned,<sup>6</sup> and an alternative model, which does not invoke superfluidity in a monolayer, has been proposed.<sup>7,8</sup>

A central issue involves the uniformity and mode of growth of the films. Traditional belief holds that films of uniform thickness can be deposited monotonically with increasing pressure up to saturation. However, recent studies show that many adsorbate-substrate combinations can form uniform films only up to thicknesses of a few atomic layers, and then bulk condensation occurs.<sup>9</sup> This type-II or Stranski-Krastanov<sup>10</sup> mode of growth has been observed in  $^3\text{He}$ -graphite films by Van Sciver and Vilches,<sup>11</sup> and in  $^4\text{He}$ -graphite by Polanco, Quateman, and Bretz.<sup>12</sup> In addition to these thermal measurements, neutron scattering from  $^4\text{He}$ -graphite shows the appearance of a bulk-liquid- $\text{He-II}$  roton-scattering peak beginning at a small number of layers.<sup>13</sup> The present study, which also examines other substrates, is based on vapor-pressure measurements.

The nature of helium films is important not only to the question of two-dimensional superfluidity but also to the more general thermodynamics of adsorption and growth.<sup>7,14</sup> In the case of helium on graphite, one has a very well-characterized system, whose properties are relatively accessible to a variety of thermodynamic and microscopic techniques, and it can be readily studied over an effectively wide range of temperature. It involves relatively simple interactions and therefore should be useful as a model sys-

tem for theoretical study.

Several previous studies of the vapor-pressure isotherms of helium on graphite substrates have been reported.<sup>15-17</sup> Their results and other relevant experiments are discussed in the text.

### II. EXPERIMENTAL DETAILS

The apparatus consisted of a sample cell in a variable-temperature cryostat, and a gas-dosing and pressure-measurement system. The cell temperature was determined from the vapor pressure of liquid helium<sup>18</sup> in a small reservoir to which the cell was thermally anchored. The dosing and pressure-measurement system contained a series of calibrated volumes, and pressures were measured with high-sensitivity capacitance gauges.

The vapor pressures were subject to appreciable thermomolecular corrections at low pressures. The appropriate corrections were calculated from a numerical integration of the Weber-Schmidt equation, with McConville's empirical parameters for stainless-steel capillaries.<sup>19</sup>

The experimental cells were individually made, of quartz or Pyrex glass, for each of the adsorbate samples. Each filled cell was baked and pumped, typically overnight, at 600 to 900 °C, then sealed with a magnetic break seal, and mounted in the cryostat, connected to the gas-dosing system and leak checked before opening the break seal.

The adsorption areas of the samples were relatively low, so that careful corrections for quantity of adsorbate in the gas phase were necessary. The fraction of adsorbate in the gas phase was dominant near saturation pressure and temperatures above about 1.6 K. Gas densities were corrected with important second virial coefficients,<sup>20</sup> but third-order corrections were unnecessary.

The adsorbent samples were as follows: exfoliated graphite foam, uncompressed exfoliated graphite powder, crystalline MgO powder, and Mylar sheet. The graphite foam and powder, like Grafoil, are produced from graphite crystals by chemical exfoliation, and are marketed by the Union Carbide Corporation. Foam and powder are less dense than Grafoil, uncompressed powder having density  $<0.01 \text{ g/cm}^3$ , while the density of foam is approximately  $0.1 \text{ g/cm}^3$ . They have comparable specific adsorption areas, about  $25 \text{ m}^2/\text{g}$ . In contrast to Grafoil, they have no preferred orientation. We chose these two low-density products over Grafoil in order to reduce the tendency for capillary condensation, owing to their larger average pore size. According to the density and specific area of foam, it is composed of pores of average dimension exceeding  $2 \times 10^{-4} \text{ cm}$ . In Grafoil the mean separation between laminae is about  $5 \times 10^{-6} \text{ cm}$ . Both foam and uncompressed powder have excellent adsorption uniformity.<sup>21,22</sup>

The MgO was a sample of MgO smoke prepared by ignition of Mg metal in air and subsequent heat treatment to  $800^\circ\text{C}$  in vacuum overnight. This treatment has been shown<sup>23</sup> to produce a powder of cube crystals of  $\sim 1000\text{-\AA}$  linear dimension, and very good adsorption uniformity.

The Mylar consisted of a stack of 2256 4.5-cm-diam disks cut from  $69\text{-}\mu\text{m}$ -thick sheet. It was enclosed in a close-fitting copper chamber sealed with epoxy cement. It was not baked, but only pumped at room temperature for two days under high vacuum.

In addition to these substrates we studied  $^4\text{He}$  adsorption on the foam preplated with one monolayer of krypton.

Figures 1–3 present Kr and Ar isotherms on graphite foam at 77 K. Our studies with the small (0.78-g) sample of foam used in the  $^4\text{He}$ -adsorption work show the formation of at least four distinct steps in Kr adsorption (Fig. 1), similar to the results obtained on exfoliated graphite powder.<sup>24</sup> A more detailed study of the rise of the second step, illustrated in Fig. 3, was taken with a larger sample from the same block of foam.<sup>25</sup> The nearly vertical riser indicates a first-order phase change (second-layer incommensurate-solid–two-dimensional gas<sup>26</sup>) on a highly uniform surface. On an ideal uniform substrate the riser would be vertical, but imperfections of various kinds destroy verticality in real systems. If we attribute the finite slope to size effects as has been done in the case of  $\text{N}_2$  films on Grafoil<sup>27</sup> and Ar films<sup>28</sup> on  $\text{CdCl}_2$ , the effect can be analyzed to yield an estimate of the dimensions of the uniform domains on the surface. In this way we obtain an average domain radius of  $600 \text{ \AA}$ , equal to the dimensions estimated for  $\text{CdCl}_2$  domains, and 3 to 6 times greater than those of Grafoil and Papyex<sup>29</sup> and somewhat greater than those of ZYX exfoliated single crys-

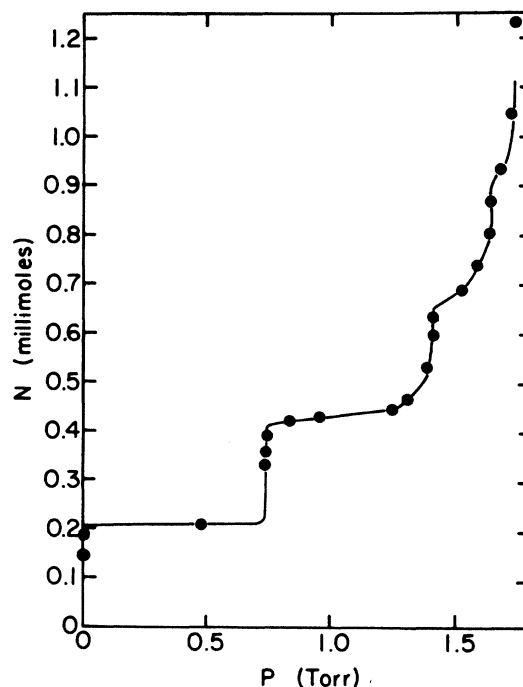


FIG. 1. Adsorption of Kr on graphite foam at 77 K.

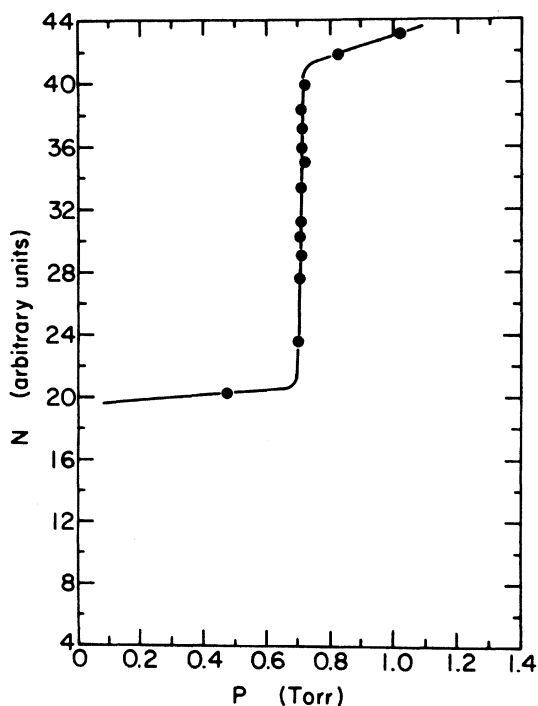


FIG. 2. Adsorption of Kr on graphite foam at 77 K: detailed examination of the second step (Ref. 25).

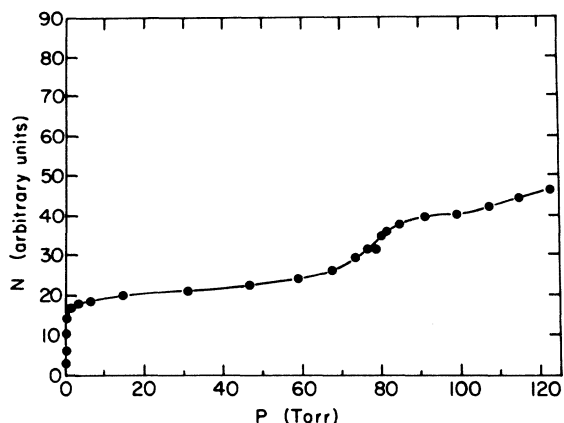


FIG. 3. Adsorption of Ar on graphite foam at 77 K.

tal.<sup>30,31</sup> This indication of the superior uniformity of graphite foam over Grafoil is consistent with the recent results of Millot on Ar adsorption<sup>21</sup> and of Larher,<sup>22</sup> who studied  $\text{N}_2$ .

The sharp step structure also provides a basis for a precision gauge of adsorption area. Previous studies have shown that the Kr isotherm on graphite foam at 77 K is nearly horizontal between 0.1 and 0.6 Torr, the coverage varying by about 4% over this interval. Therefore an equilibrium pressure within the range is a sensitive gauge of the relative coverage, which can be related to the density of the completed first-layer-incommensurate solid.<sup>26</sup>

Figure 3 shows an Ar isotherm on the foam sample taken at 77 K. In contrast to the Kr, this isotherm shows no sharp structure, although rounded steps are evident. The absence of a vertical or nearly vertical riser is consistent with the absence of a two-phase coexistence regime in Ar on graphite at this temperature.<sup>32</sup> Nevertheless, the Ar isotherm can be utilized as a qualitative gauge of substrate uniformity. The "knee" of the isotherm, between about 1 and 10 Torr, indicates that the completion of the first monolayer takes place within a relatively narrow range of coverage. The corresponding feature on Grafoil is about twice as broad, indicating that monolayer completion is less well defined. This is consistent with the more quantitative comparison obtained from Kr adsorption, which is discussed above.

We also measured the areas of the exfoliated graphite powder and the MgO powder by Kr adsorption. They showed clear step structure, but we did not follow this low-coverage behavior as carefully as the isotherm on graphite foam and hence cannot give a quantitative comparison of substrate uniformity.

The Mylar substrate proved very slow to reach equilibrium in Kr adsorption and therefore we estimated its area by  $\text{N}_2$  adsorption. We believe that the long equilibrium times are due to a combination

of the low surface mobility of Kr at 77 K, its low vapor pressure at monolayer densities, and the tight packing of the Mylar sheets, which greatly reduced gas transport.  $\text{N}_2$ -adsorption equilibrium times were much shorter, due to higher vapor pressure and probably, also, the higher surface mobility of the  $\text{N}_2$  at these temperatures. The  $\text{N}_2$  isotherm showed no sharp distinguishing features, but only a smooth sigmoid curve with a broad "knee." The shape is typical of relatively heterogeneous materials.<sup>33</sup> The area as measured by the "Point-*B*" method<sup>33</sup> agreed well with the geometric area.

### III. RESULTS AND ANALYSIS

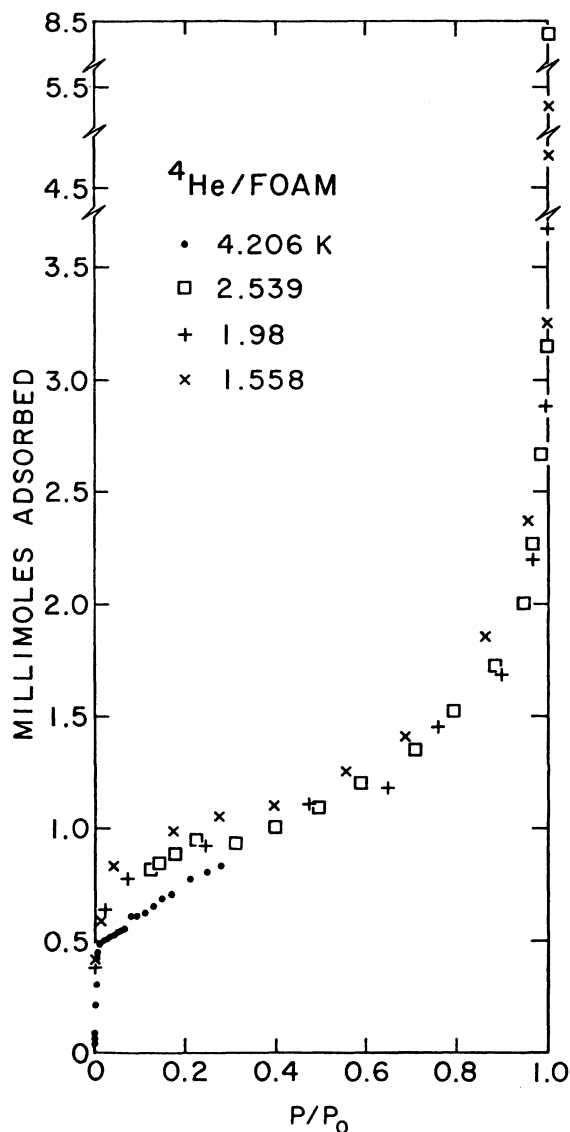
Our most extensive studies were on the foam substrate. In Fig. 4 we present the family of  $^4\text{He}$  isotherms at several temperatures. Since our interest was on the multilayer region above two layers we did not examine low coverages, except for the 4.2-K isotherm, and hence the first two layers were not resolved. Several features are evident. The trends are similar in that they break away from the low-pressure region rather suddenly, at about the same coverage. According to the area measurement by Kr adsorption and the known densities of the first and second  $^4\text{He}$  layers  $0.115$  and  $0.082 \text{ \AA}^{-2}$ , respectively,<sup>13,15,34</sup> the break occurs near two layers. The pressure rises rather rapidly until, at a coverage of four to five layers it slows considerably. At a coverage of about eight layers the pressure reaches a value which remains sensibly constant up to at least 30 layers. The isotherm shows no layer structure in the explored region, which can be attributed to the relatively high temperatures compared to the variations in the heat of adsorption between adjacent layers above the second layer.

The overall shape of the isotherms indicates type-II growth. As noted in the Introduction, type-II growth has been deduced from calorimetric studies but had not been seen in vapor pressure isotherms.

By way of comparison with models of uniform growth, in Fig. 5 we show the data for one of the isotherms together with the Frenkel-Halsey-Hill (FHH) equation<sup>35-37</sup>

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

calculated for two different values of the van der Waals potential  $\alpha$ . The larger value is the average of  $^4\text{He}$ -graphite measurements of quite different kinds.<sup>38</sup> Elgin and Goodstein<sup>16</sup> deduced that the single atom binding in the first layer is  $143 \pm 2 \text{ K}$  from analysis of thermodynamic data of monolayers on Grafoil. Molecular-beam scattering from single-crystal surfaces has yielded two values in close agreement: Boato, Cantini, and Tatarek<sup>39</sup> obtained  $136 \pm 3 \text{ K}$ ,

FIG. 4. Adsorption of  $^4\text{He}$  on graphite foam.

and Derry, Wesner, Carlos, and Frankl<sup>40</sup> have measured  $140 \pm 2$  K. Herb and Dash<sup>41</sup> estimated 130 K from isotherms over a limited region. Sabisky and Anderson<sup>42</sup> obtained a much lower value, 65 K, from an analysis of onset experiments utilizing the Ginzburg-Pitaevskii model of superfluidity.<sup>43</sup> It is clear from Fig. 5 that neither value of  $\alpha$  describes the data; indeed, no single value for  $\alpha$  in Eq. (1) can yield agreement with the data. This behavior is consistent with the predictions of a recent theory of the helium film-graphite surface interaction,<sup>44</sup> discussed in Sec. III.

The constancy of pressure at higher coverages clearly indicates that bulk is present at a mean cover-

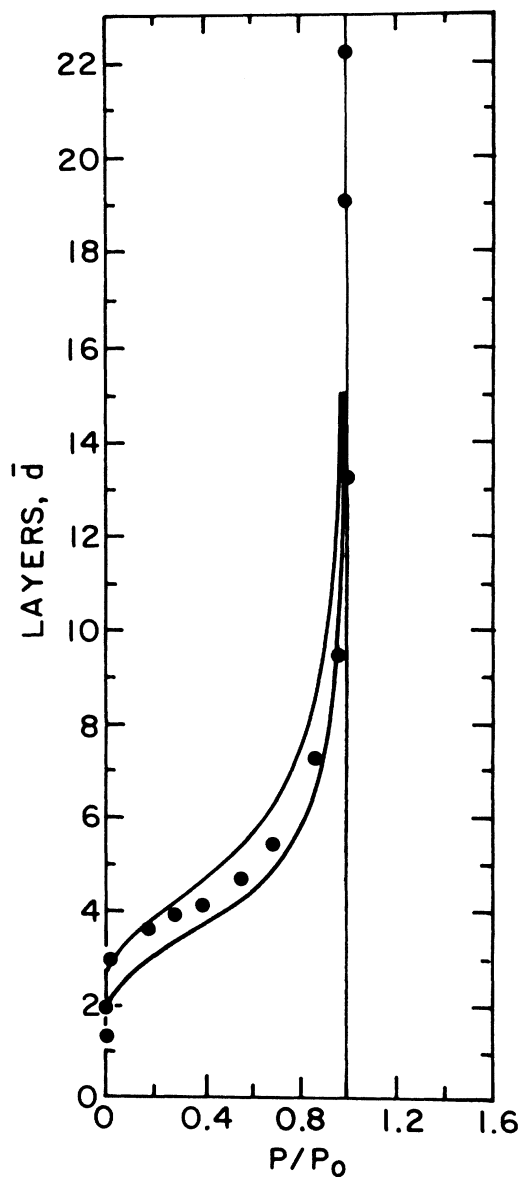


FIG. 5. Adsorption of  $^4\text{He}$  on graphite foam at 1.55 K. The two solid curves are calculated according to the Frenkel-Halsey-Hill formula, Eq. (1) (Refs. 34–36) for first layer binding energies  $65k_B$  (lower curve) and  $143k_B$ .

age of eight layers. Moreover, it is likely that the local thickness at which bulk first appears is considerably less. When bulk first appears it must form within crevices and other regions of negative curvature, so that the surface energy due to the liquid-vapor interface can be minimized. This "capillary-condensed" liquid has a surface with a larger radius of curvature but it is still negative. As a consequence the vapor pressure of the gas in equilibrium with the surface is lowered below the  $P_0$  of the flat surface

liquid, with relative change approximately given by<sup>45</sup>

$$\delta P/P_0 = -2\gamma v/r_m kT, \quad (2)$$

where  $\gamma$  is the interfacial tension, which is assumed to be size independent,  $v$  is the molecular volume, and  $r_m$  is the mean radius of curvature of the surface. In addition to the curvature effect there is a substrate attractive term. If the distance between the substrate and the surface locally is  $d$ , not so large as to involve retardation, the reduction of chemical potential<sup>46</sup> is  $\alpha/d^3$ . The two terms can be combined by noting that the relative pressure change in Eq. (2) can be written in terms of the chemical potentials of the gas in equilibrium with the surface, if the pressure is sufficiently low:

$$\mu_g(P, T) = kT \ln(P\lambda^3/kT), \quad (3)$$

where  $\lambda = h(2\pi mkT)^{-1/2}$  is the thermal de Broglie wavelength. The curvature effect and substrate attraction are additive in their effects on the chemical potential. The resulting change in vapor pressure, using Eq. (3) is given by

$$kT \ln(P/P_0) = -2\gamma v/r_m - \alpha/d^3. \quad (4)$$

Equation (4) is equivalent to a relation given previously by Cole and Saam.<sup>47</sup>

Equation (4) relates the vapor pressure of the system to the local thickness and curvature. The pressure is uniform in the vapor (far from the substrate) although  $r_m$  and  $d$  vary from place to place. In narrow crevices and inside corners, where the liquid tends to condense the curvature term tends to dominate, and in the thinner and flatter regions the attractive term becomes more important. Their combined action causes liquid to be formed at pressures below  $P_0$ . The quantity that is formed depends on the relative pressure, the values of  $\alpha$  and  $\gamma$ , and the internal geometry of the adsorbent. On finely porous or fissured and rough surfaces capillary condensation will be relatively important, and the isotherm will have a significant rise at pressures below  $P_0$ . On very flat surfaces there are few regions where the liquid tends to condense, hence the liquid that does exist is in larger volumes. The local  $r_m$  and  $d$  are then proportionately greater, and therefore the isotherm rises more abruptly close to  $P_0$ . Thus we see that the shape of a type-II isotherm in the neighborhood of  $P_0$  should permit a kind of mapping of the internal structure of the adsorbent.

An estimate of the critical thickness  $d_c$  at which liquid is first formed can be obtained by applying Eq. (4) to the foregoing argument. We want to analyze the data to obtain some measure of the typical size  $l$  of liquid volumes trapped in pores and crevices, and then compare this size to the average film thickness  $\bar{d}$ . It can be expected that at  $\bar{d} > d_c$  the typical size will increase much faster than  $\bar{d}$ . The manner of this

increase cannot be predicted since it depends on many factors, including the internal geometry of the adsorbent,<sup>47</sup> its adsorption heterogeneity, and the equation of state of the film<sup>7,14</sup> near  $P_0$ . However, in general we expect some significant increase in the neighborhood of  $l = \bar{d} = d_c$ , a signal of liquid formation. To calculate  $l$  by Eq. (4) we assume that the local radius of curvature  $r_m$  and the thickness  $d$  of the liquid are comparable and can be represented by the single parameter  $l$ . Thus we obtain from Eq. (4)

$$kT \ln P/P_0 = -2\gamma v/l - \alpha/l^3. \quad (5)$$

The approximation involved in equating  $l$  and the local  $d$  is very rough and can be quite inappropriate in some instances. However, in the systems of interest here we find that at  $\bar{d} = d_c$  the attractive term in Eq. (5) is much smaller than that due to surface curvature, hence the liquid is effectively characterized by just the single parameter associated with surface curvature.

In Fig. 6 is shown the characteristic size  $l$  as a function of coverage, computed from one of the isotherms of <sup>4</sup>He on graphite foam. For this calculation we used the value<sup>44</sup>  $\alpha/k = 44$  K and the value of surface tension appropriate to each temperature.<sup>48</sup> Here we see a significant rise of  $l$  to values well above  $\bar{d}$  beginning at about 10 Å. In the range 10 Å <  $\bar{d}$  < 17 Å the value changes from  $l = \bar{d}$ , and the slope in-

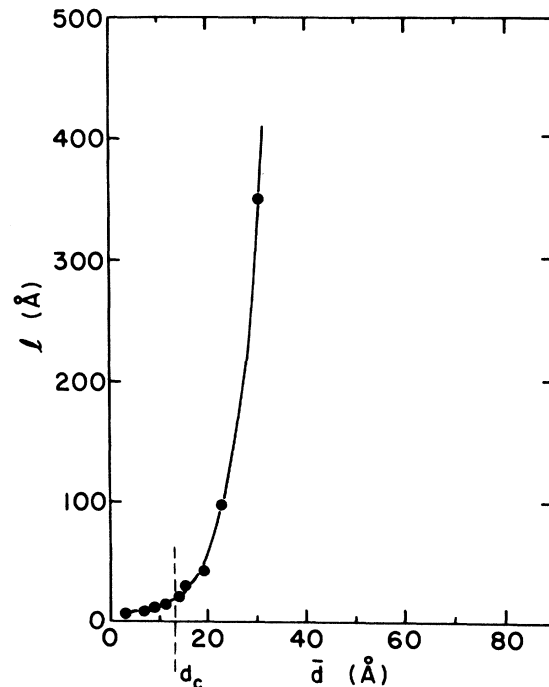


FIG. 6. Characteristic dimension  $l$  of bulk-liquid <sup>4</sup>He condensed in pores and crevices of graphite foam as a function of mean thickness, at  $T = 1.98$  K.

creases by a factor of 4. We identify these changes as due to the onset of liquid formation, and estimate the critical thickness on the graphite foam at 1.55 K in this range; i.e.,  $d_c = 13.5 \pm 3.5 \text{ \AA}$ . To convert to layer equivalents we use the values  $d_1 = 2.95 \text{ \AA}$ ,  $d_2 = 3.49 \text{ \AA}$ , and  $d_n = 3.58 \text{ \AA}$  for  $n > 2$ , derived from the densities of the first and second completed layers on graphite and the density of bulk liquid.<sup>13, 15, 34, 49-51</sup> Accordingly, the critical thickness is equivalent to  $4.0 \pm 1.0$  layers. The other isotherms on graphite foam and on exfoliated graphite powder show similar behavior, with large accelerations of the computed  $l$  in the range  $\bar{d} \leq l \leq 2\bar{d}$ . Adopting this criterion for the estimate of critical thickness, we obtain a consistent set of values of  $d_c$ , as listed in Table I. The average of all of the graphite results is  $4.0 \pm 0.3$  layers.

The isotherm data can be analyzed in another, equivalent manner by differentiating adjacent isotherms so as to obtain the isosteric heat of adsorption  $q_{st}$ , which is in general related to the vapor pressure by<sup>52, 53</sup>

$$q_{st} = kT^2 \left( \frac{\partial \ln P}{\partial T} \right)_n \quad (6)$$

In Fig. 7 we show  $q_{st}$  obtained from isotherms on foam and on exfoliated graphite powder. Here we see as in the isotherms directly a gradual approach to the bulk value, which is reached at a thickness of seven or eight layers. However, the initial formation of bulk liquid probably takes place considerably earlier, consistent with the estimate obtained from the isotherms. For if we differentiate Eq. (5) with respect to  $T$  according to Eq. (6), we obtain

$$q_{st} = (q_{st})_0 + \frac{2\gamma v}{l} + \frac{\alpha}{l^3} - \frac{2Tv}{l} \left( \frac{\partial \gamma}{\partial T} \right), \quad (7)$$

where  $(q_{st})_0$  is the bulk value. The last term is relatively unimportant at low temperatures and the contributions due to the possible temperature dependence of  $d_c$  are neglected, but the first two are signi-

TABLE I. Critical film thickness for bulk-liquid formation.

Substrate	$T$ K	$d$ (layers)
Graphite foam	1.37	$3.7 \pm 1.0$
Graphite foam	1.55	$4.0 \pm 1.0$
Graphite foam	1.98	$3.8 \pm 0.8$
Graphite foam	2.54	$4.8 \pm 1.5$
Exfoliated graphite powder	1.37	$3.9 \pm 0.6$
Kr-plated graphite foam	1.56	$2.4 \pm 0.5$
MgO cube crystals	1.46	$1.5 \pm 0.1$
Mylar	1.98	$3.7 \pm 0.7$

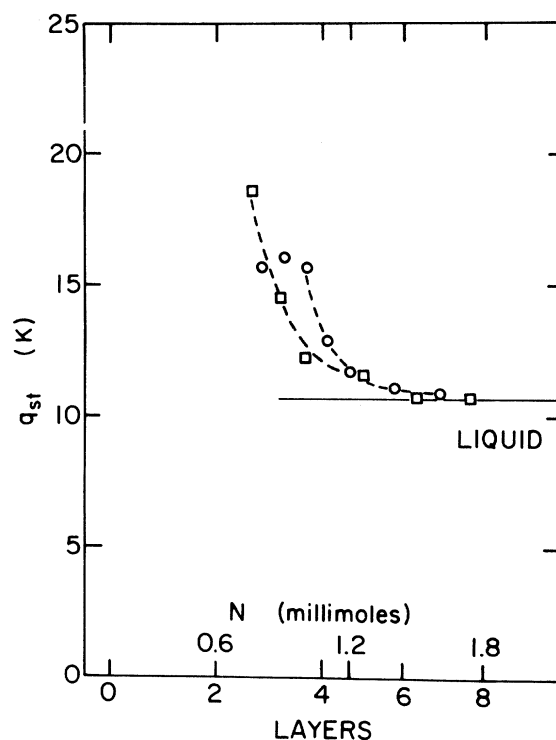


FIG. 7. Heat of adsorption of  $^4\text{He}$  on graphite between 1.3 and 2.5 K.  $\circ$  exfoliated graphite powder;  $\square$  graphite foam. The solid line corresponds to the latent heat of bulk liquid.

ficant for all  $T$  and moderate  $l$ . At  $l = 4$  layers their combined contribution is about 3 K. This is comparable to the excess of the experimental value over  $(q_{st})_0$  at that coverage, and hence we can conclude that this way of examining the data yields the same estimate for  $d_c$  as the direct analysis of the isotherms.

Krypton plating produces important changes in the helium adsorption, the shapes of the isotherms remaining generally unchanged, but shifted to lower coverages. An analysis of the plated substrate according to the same procedure, followed for the unplated sample [but with potential energy 18 K corresponding to  $^4\text{He}$  on solid Kr (Ref. 54)] indicates a critical thickness at 1.56 K of  $2.4 \pm 0.5$  layers, a reduction of more than one full layer.

The MgO isotherm is shown in Fig. 8. It is compared to Eq. (1) with points calculated according to the theoretical<sup>54</sup> van der Waals potential 28.6 K for this material. Just as for the isotherms on graphite, we find the FHH equation in disagreement with the experimental results. The data indicate liquid formation takes place by a coverage amounting to four or five layers. The results were analyzed for the characteristic dimension  $l$ , and yielded the curve shown in Fig. 9. Here we found a sharper onset of liquid formation than on graphite, perhaps due to a smoother

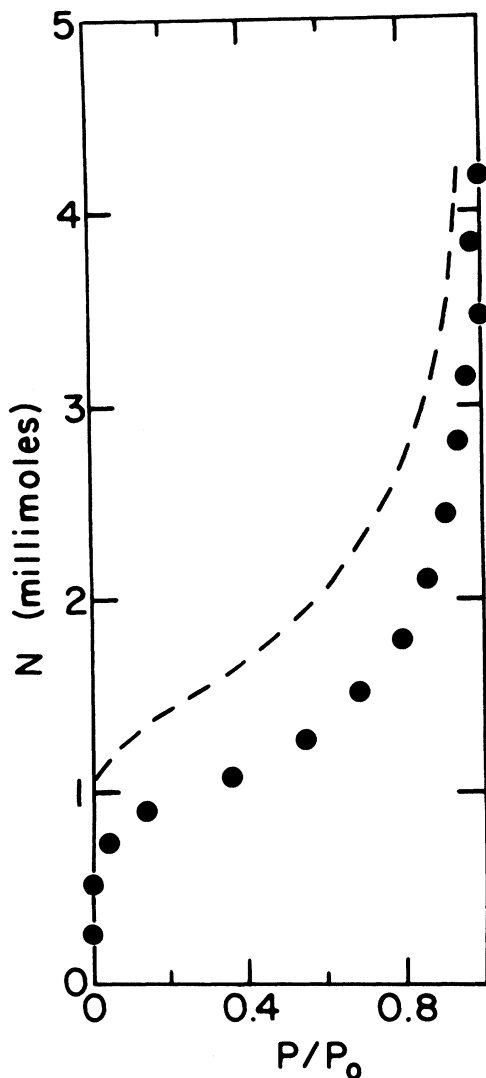


FIG. 8. Adsorption of  $^4\text{He}$  on MgO crystals at 1.46 K. The solid line is calculated from Eq. (1) with binding energy 28.6 K in the first layer.

surface texture with fewer crevices. The critical thickness is the lowest we found in these experiments:  $1.5 \pm 0.1$  layers.

The Mylar isotherm at 1.98 K is shown in Fig. 10. It is seen to have a shape similar to the others, in that it tends to meet the  $P = P_0$  axis at a large angle, then curves upward and reaches  $P_0$  at a higher coverage. As in the previous cases the overall behavior indicates type-II growth. By contrast we compare isotherms calculated according to Eq. (1), computed for two different values of the binding energy, in Fig. 11.

The lower value is interesting because it is comparable to the van der Waals potential of He films on a variety of ionic solids, semiconductors, and metals,

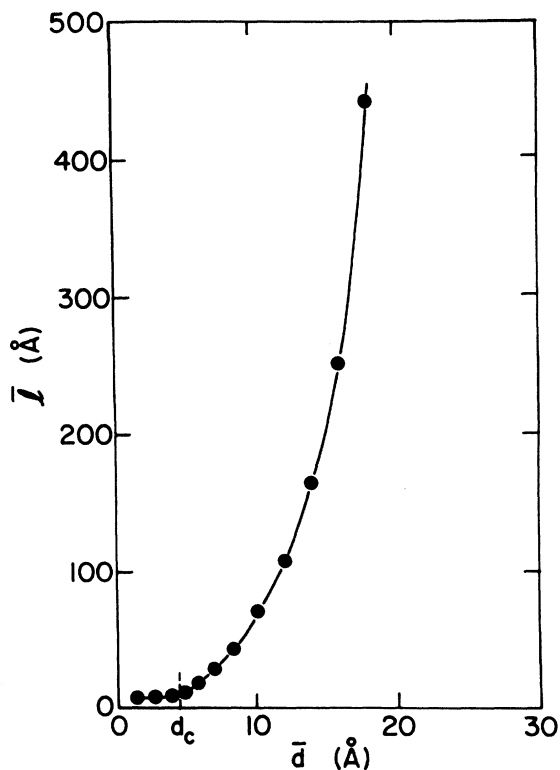


FIG. 9. Characteristic dimension  $l$  of capillary condensed liquid  $^4\text{He}$  in MgO crystalline powder at 1.46 K.

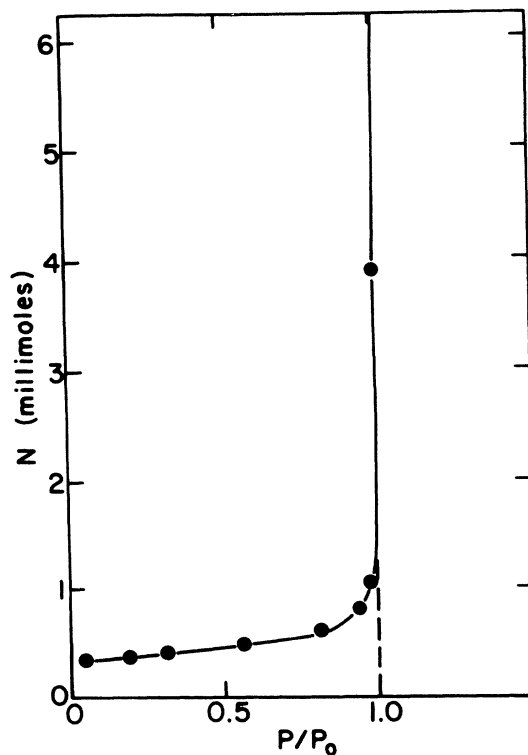


FIG. 10. Adsorption of  $^4\text{He}$  on Mylar at 1.98 K.

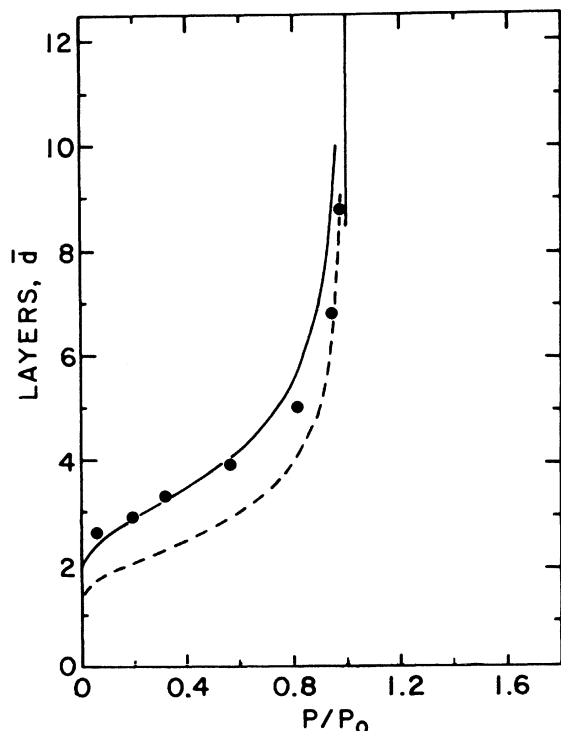


FIG. 11. Comparison of Mylar isotherm at 1.98 K with the isotherm of a liquid slab, Eq. (1). The dashed curve is calculated for first-layer binding energy 27 K; the solid curve for 75 K.

calculated by Sabisky and Anderson.<sup>54</sup> The van der Waals potential of Mylar has not been given, but it would seem to be in the range of typical materials, for which the largest theoretical value quoted is 49 K. However, it is clear that the value which would best approximate the data at moderate coverages, i.e., of a few multilayers, is much larger. The value which gives the correct thickness at  $P/P_0 = 0.5$  is 75 K, about 3 times greater than the typical computed value. As is clear from Fig. 11, no single value of the potential, with a fixed exponent of the thickness in Eq. (1), can represent the actual behavior, and analysis similar to that performed on the other isotherms indicates that the critical coverage  $d_c = 3.7 \pm 0.7$  layers.

### III. DISCUSSION

Our determination of type-II growth in <sup>4</sup>He-graphite agrees with the earlier conclusions based on indirect evidence,<sup>7</sup> and with the recent direct results of Polanco, Quateman, and Bretz,<sup>12</sup> and Polanco and Bretz.<sup>49</sup> We disagree, however, in the value of the critical thickness, given in the earlier report,<sup>12</sup> our result being about one layer lower than theirs.

Although it is conceivable that this difference is a real effect of the two different substrates, we think it may be due to their neglect of size effects, of the type discussed above.

The critical coverage found in the present study is approximately equal to the value  $d_{\text{onset}} = 3.5$  layers deduced from an analysis of superfluid onset on graphite.<sup>8</sup> It therefore lends additional weight to the clustering and percolation model,<sup>7</sup> which was developed partly to explain the superfluid films. Nevertheless, it should be emphasized that no study, including this one, has directly demonstrated that clustering actually does occur in <sup>4</sup>He-graphite. Peierls<sup>14</sup> has shown that a variant of type-II growth may involve an accession to saturation pressure in a uniform film at finite thickness. Our analysis in this study has assumed that clustering does occur, and makes plausible estimates of the characteristic sizes of liquid volumes but this treatment cannot be said to be a proof of clustering. Proof of clustering will require direct observation, as, e.g., by low-angle neutron scattering.

Apart from the question of clustering, our isotherms show that the FHH law is not obeyed at intermediate coverages, approximately three to ten layers. Since the FHH law is traditionally used to analyze vapor-pressure data to obtain the thicknesses of adsorbed helium films, its failure in the present study raises serious questions about the interpretations of many experiments. Our findings with regard to the FHH equation are consistent with several other types of evidence, discussed below.

The theoretical basis for the FHH law is the assumption that the surface of the film has the thermodynamic properties of the surface of bulk fluid at the same temperature,<sup>55</sup> i.e., that the partial entropy  $(\partial S/\partial N)_T$  is identical to that of the bulk. In this event, the chemical potentials differ by the external potential only. But since experiments universally indicate that thin films are qualitatively different from bulk liquid, this removes the theoretical basis for the law, at least in the range of a few layers. At higher coverage if clustering occurs, the film is composed of small liquid droplets, where curvature effects can dominate over the influence of substrate fields. Therefore the regime in which the FHH law should hold is restricted to "thick films," above the point where the droplets coalesce into a uniform thickness sheet. The coverage at which this occurs depends on the density of nucleating sites, but is in any case several times the clustering coverage. Our experimental resolution was inadequate to test the law in this regime.

A series of experiments some years ago by Sabisky and Anderson<sup>54</sup> examined adsorbed He films over a wide range of thicknesses. The measurements were based on an acoustic interferometric technique to



measure the resonances of films adsorbed on rare-earth halides. Their conclusions were that the FHH law was very closely followed in the range  $\sim 10\text{--}100$  Å, above which the exponent of  $d$  increased gradually from 3 to 4, due to retardation. The magnitude of the experimental van der Waals parameter was found to be in agreement with the theoretical value calculated from the Lifshitz theory.<sup>46</sup> Our results are clearly at variance with these experiments, but several points should be emphasized. (i) The substrates examined in the two studies are different, and although we obtained similar results from all of the surfaces we studied, and Sabisky and Anderson obtained similar results in all of theirs, it is conceivable that the behavior of He films on the two classes of substrates are qualitatively different. (ii) The principal ranges of sensitivity of the two techniques are different, vapor pressure isotherms being most sensitive to relatively low thicknesses up to  $\sim 10$  layers, while the acoustic technique is best applied to thicker films. (iii) The acoustic experiments were subject to uncertainties due to phase shift and dispersion corrections which were of major importance at thicknesses below about four layers, and which remained significant to much greater thicknesses.

A new calculation of the van der Waals interaction between helium and a graphite surface has been reported by Vidali, Cole, and Schwartz.<sup>44</sup> Using recent molecular-beam-scattering data, they compute the value  $\alpha/k = 44.0 \text{ K (layer)}^3$  at sufficiently large distances for the inverse  $d^3$  law to hold. The simple law fails at smaller distances. If the law is assumed to hold, but with a thickness-dependent potential,  $\alpha/k$  rises as  $d$  decreases, reaching a value  $\sim 100 \text{ K (layer)}^3$  for thin films.<sup>56</sup> This is what our data show.

Apart from the deviations from the FHH law that

can be expected for uniform thickness films at low to moderate coverage, major deviations can be caused by type-II growth. We have no information on the mode of growth of helium films on substrates other than those examined in this study, nor can we draw any conclusions about possible differences between the behavior of  $^3\text{He}$  and  $^4\text{He}$  on the substrates studied. Recent experiments have shown that graphite and MgO substrates affect the solidification of the two isotopes in qualitatively different ways, suggesting that mechanisms related to those underlying the modes of film growth are also operative in solidification adjacent to a wall.<sup>57-59</sup>

We have some indications of surface specificity in the present data. There is a definite trend toward lower  $d_c$ 's on the lower binding substrates, consistent with the empirical rule that wetting is less likely on weaker substrates.<sup>60</sup> According to this rule, the films on MgO should have  $d_c$  greater than on the Kr-plated graphite. It is possible that this evidently decreased wetting could be due to the strong textural relief of the MgO (100) surface, and the mismatch between the density and symmetry of its sites and that of a solid-helium monolayer.

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