

## Integral and Nonintegral Layer Formation in Multilayer Growth of Solid $^4\text{He}$ on Grafoil

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With use of a differential adsorption technique combined with acoustics, we have investigated the layered growth of solid  $^4\text{He}$  on Grafoil from the pressurized liquid phase. At low pressures, we found a first-order phase transition each time a layer was completed, whereas at high pressures the transitions occurred near midlayer, at a coverage characteristic of an epitaxial phase of He on graphite. Our results support the predictions of recent theories of multilayer growth.

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The study of atomically thin layers of He on various substrates has provided us with a wealth of information<sup>1</sup> regarding melting in two-dimensions (2D),<sup>2</sup> epitaxial growth,<sup>3</sup> and 2D superfluidity.<sup>4</sup> As additional solid is formed above a monolayer many exciting phenomena are predicted to occur, such as distinct layer-by-layer growth with a first-order phase transition taking place at a completion of each layer,<sup>5-7</sup> different modes of growth depending on the surface being smooth or rough on an atomic scale,<sup>6</sup> and a possibility of first-order phase transitions occurring at a nonintegral layer number.<sup>6</sup> Unfortunately, as one adds He to the system, bulk liquid nucleates when the surface coverage exceeds a few atomic layers. Further investigation of the surface region becomes exceedingly difficult, because in a typical experimental geometry the number of atoms strongly influenced by their substrate is very small compared with the number contained in the bulk. Therefore, the discovery of new features in the propagation of fourth sound in Grafoil,<sup>8</sup> which were interpreted in terms of layer by layer growth of solid from the pressurized liquid  $^4\text{He}$  phase, opened a door in that seemingly inaccessible direction. As expected, the experiment provoked several important questions. First, the surface attracts the atoms via the van der Waals potential  $V(n) = -\alpha'/n^3$  where  $\alpha'$  is a constant estimated at 44 K for He on graphite,<sup>9</sup> and  $n$  denotes the distance from the graphite surface in solid layer units. Adsorption experiments indicate<sup>10</sup> that some 4-5 layers are adsorbed onto the surface by the time bulk liquid  $^4\text{He}$  appears around 1 K. The fourth-sound experiments<sup>8</sup> indicate a nucleation of several additional solid layers from the liquid phase as the pressure is raised near 1 K. In contrast, the calculated attractive potential for these layers is much less than 1 K/atom, which would deem the nucleation of that much solid highly unlikely. Second, the way in which the fourth sound couples

to the surface is not clear. As the information extracted from the acoustic data regarding the growth of solid is very much model dependent, different models for the coupling of the sound to the surface yield different pictures of the growth process.<sup>8,11,12</sup> To try to clarify some of these points, we decided to measure the solid adsorption directly, while simultaneously performing acoustic measurements in the same cell.

Conventionally, adsorption isotherms are obtained through the measurement of the amount of matter that "disappears" from the gaseous phase when added to the system, due to adsorption onto an initially bare surface. In contrast, we begin here with a cell completely filled with liquid and with several layers of solid already adsorbed onto the Grafoil surface. The main difficulty in our experiment stems from the very small difference in the molar volumes of liquid and solid  $^4\text{He}$ , which makes it hard to separate, given a total amount of  $^4\text{He}$  added to the cell, the part that compresses the liquid from the part that solidifies. To circumvent this problem we used two cells, having closely matched internal volumes and identical fill lines with both cells and fill lines anchored thermally in an identical fashion. This arrangement allowed us to eliminate the systematic errors introduced by pressure drifts caused by temperature changes along the cell fill lines. One cell, referred to as the reference cell, had an internal volume  $V_R$  but a negligible surface area. The other, referred to as the Grafoil cell, was a cylindrical sound resonator packed with Grafoil disks. The total surface area of the Grafoil was in excess of 400 m<sup>2</sup>. We denote by  $V_G$  the volume occupied by the liquid at  $P=0$  with several layers of solid already adsorbed onto the surface. The precise value of  $V_G$  was determined from the data for each temperature. The predominant acoustic mode of the resonator was a mixture of first and fourth sound,<sup>13</sup> because of the inability

to pack the Grafoil without severe loss of surface area. We found that this acoustic mode exhibited features similar to those observed in the fourth-sound experiment.<sup>8</sup> Because of cryogenic constraints, data were taken while reducing the pressure in the cell from near solidification to zero in small steps. In each step, a known number of moles,  $\Delta n_G$ , was removed from the Grafoil cell,

$$\Delta n_G - \Delta n_R = \frac{V_G - V_R}{V_L} \kappa \Delta P - \frac{V_S}{V_L} \kappa \Delta P n_s + \frac{V_L - V_S}{V_L} \Delta n_s. \quad (1)$$

The first term on the right-hand side of Eq. (1) is due to imperfectly matched internal open volumes, where  $V_L$  is the molar volume of bulk liquid and  $\kappa$  its compressibility.<sup>14</sup> The second term represents the decrease in  $V_G$  from its value at  $P=0$  due to the presence of  $n_s$  moles of solid with a molar volume  $V_S$ , taken here as the bulk value of melting pressure. The last term gives the total amount of solid,  $\Delta n_s$ , which melts in the process of one such step. Note that out of the total amount that melts,  $\Delta n_s$ , the fraction actually removed from the cell is only  $\Delta n_s (V_L - V_S)/V_L$ , as one needs to remove only that much to change the density from that of a solid to a liquid. By summing  $\Delta n_s$ , we obtained the adsorption isotherms shown in Fig. 1. As the number of adsorbed layers in the liquid filled cell at  $P=0$  is not known,  $V_G$  was determined by imposing the condition that each solid layer contains the number of moles appropriate to the known surface area.

It is immediately evident that the 0.1-K isotherm has more layers adsorbed than the one at 1.3 K. This reflects the low binding energy of these last layers, certainly less than 1 K/atom. The adsorption starts at very low pressures, with a whole layer completed at less than 7 bars at 1.3 K. In contrast, the fourth-sound experiment did not indicate any growth below 15 bars.<sup>8</sup> We have similarly found that none of the many acoustic resonances that were monitored reflected all of the growth features observed in the adsorption isotherm, although for each growth feature some of the resonances showed an effect. By correlating the adsorption isotherm with the acoustic data, we also found that except at very high pressure, the damping of the sound was strongest near half-layer coverage, while velocity features occurred near full layers. This is in accord with the picture presented by Adler, Kuper, and Schulman<sup>11</sup> where the damping occurs through surface fluctuations, strongest near half-layer coverage. The reason for the selective sensitivity of fourth sound to some of the growth features is not clear,

reducing the pressure in it by an amount  $\Delta P$ . As soon as equilibrium was reached, a quantity  $\Delta n_R$  was removed from the reference cell to produce precisely the same pressure change. Taking the difference between  $\Delta n_G$  and  $\Delta n_R$  subtracts out most of the change associated with the liquid phase, including, in particular, that of the fill lines. With use of thermodynamics, the remaining difference is given by

although it must have to do with the coupling between the sound and the surface. A detailed description of our acoustic measurements will be presented elsewhere.<sup>15</sup>

An important question in all adsorption studies regards the relation between external pressure and the thickness of the adsorbed phase. Previous stud-

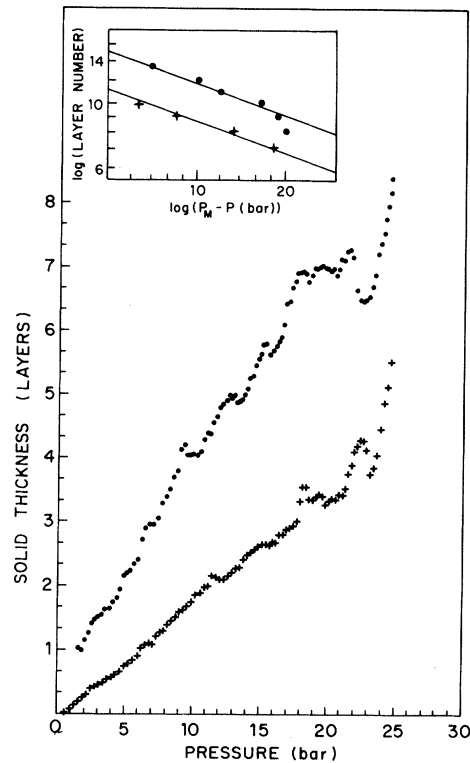


FIG. 1. Adsorption isotherms vs pressure at 1.3 K (crosses) and 0.1 K (circles). Layer numbers are counted from the  $P=0$ , liquid-filled state of the cell. For clarity, the 0.1-K isotherm was displaced vertically by one layer. Vertical scale does not apply to data taken above 18 bars, which was possibly affected by capillary condensation. Inset shows average solid thickness vs  $P_M - P$  for this data. Layer numbers in the inset were assigned to give closest fit to a  $(P_M - P)^{-1/3}$  law, shown by the solid lines.

ies<sup>8,16</sup> used a form derived from the van der Waals force, namely the so-called Franchetti relation<sup>17</sup> for the average solid thickness  $\mathcal{D}_c$ ;  $\mathcal{D}_c = \alpha / (P_M - P)^{1/3}$ . Here,  $P_M$  is the bulk melting pressure and  $\alpha$  is the van der Waals constant in units of layer  $\times$  bar<sup>1/3</sup>. According to theory,<sup>6</sup> at the completion of each layer the solid thickness equals  $\mathcal{D}_c$ . Assuming *a priori* consistency of our data with this relation allowed us to assign an absolute number to each completed layer, and thus to determine the apparent solid thickness at  $P = 0$  with the cell filled with liquid. (See inset in Fig. 1.) At 1.3 K, we found  $\mathcal{D}_c(0) \cong 6$  layers, in agreement with our determination of the decrease in  $V_G$  due to adsorbed solid at  $P = 0$ . This value is slightly higher than obtained in film studies.<sup>10</sup> A higher value follows the trend pointed out by Bienfait and others,<sup>10</sup> namely that  $\alpha$  apparently increases with coverage. For the 0.1-K data, we could not find similar consistency for any choice of layer numbers. As shown in the inset in Fig. 1, the deviations are largest at low pressure. This behavior is not understood at present. We conclude that this relation by itself cannot be reliably used to convert pressures to solid thickness.

By interpolating smoothly between the full-layer points in Fig. 1 we defined a continuous coverage, i.e., a description of the average solid thickness versus pressure with no layering involved. With this as an input, we calculated the adsorption isotherm including layering, using the theory by Weeks.<sup>6</sup> Results are shown in Fig. 2 as the solid line. The fit required one parameter,  $Y_0$ , which measures the strength of the layering term in the model Hamiltonian.<sup>6</sup> We chose  $Y_0 = 0.65$ . There are several differences between the experimental and theoretical curves. There is an asymmetry of the width in pressure between the flat and the sloped portions of the experimental isotherm. Partly, this could be attributed to surface inhomogeneity, but it may also point towards future refinements of the part of the model responsible for the layering. The apparent flattening of the experimental isotherm at high pressures is an artifact caused by capillary condensation of solid. When this takes place the open volume,  $V_G$ , decreases faster than allowed by Eq. (1), which includes only solid formation, but not the plugging of the fine pores of the Grafoil. For a different batch of Grafoil with a different porosity we obtained the data shown as the lower curve in Fig. 2. These measurements, which we extended down to about 5 bars, clearly show that high-pressure data free of problems associated with capillary condensation can be obtained. We

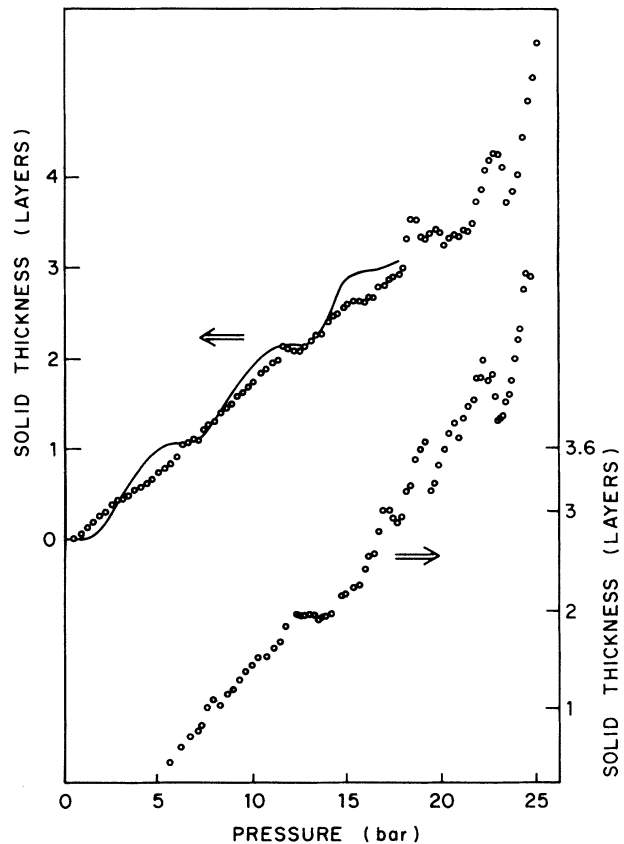


FIG. 2. Top trace: 1.3-K adsorption isotherm. Solid line shows a fit to the theory of Ref. 6. Lower trace: Data from a different sample of Grafoil at 1 K, showing high-pressure phase transitions at nonintegral layer coverage.

therefore did not correct Eq. (1) for this effect and used the data presented by the lower curve in Fig. 2 for our interpretation of the high-pressure results.

Finally, we examine the evidence for the occurrence of phase transitions associated with the solid growth. First, we observed that the 0.1-K isotherm in Fig. 1 shows small dips at the completion of layers 4, 5, and 6. These dips can be interpreted either as the melting of solid due to pressure increase, which we find quite unlikely, or else as small changes in the density of the last completed layer. These we naturally associate with the first-order phase transition predicted to occur at the completion of each layer.<sup>5-7</sup> The magnitude and sign of these changes imply a few percent decrease in the density of one layer. Such a decrease is expected if a transition is made from a denser solid phase characteristic of the layers near the graphite to the less dense bulklike solid <sup>4</sup>He. The corresponding portion of the 1.3-K isotherm did not show such dips, as expected when the temperature

is higher than the bulk roughening transition temperature.<sup>5-7,18</sup> The most novel feature of our experiment is the observation of phase transitions at nonintegral layer numbers. This is particularly evident in the data shown in the lower curve in Fig. 2, taken at about 1 K, where we find a completed layer at 17 bars, and then a large dip which occurs at about 19 bars, where the coverage is close to 0.6 of the next layer. The next large dip occurs at about the same coverage, one layer higher. Mid-layer phase transitions near the bulk roughening temperature were predicted by Weeks.<sup>6</sup> The plausibility arguments needed to explain such a phenomenon were recently put forward by Ebner, Rottman, and Wortis.<sup>19</sup> Basically, in the presence of an attractive substrate and interlayer repulsive nearest-neighbor interactions, the atoms would tend first to sit at the most attractive spots, that is in a configuration epitaxial with the substrate. As the layer is completed, the epitaxial phase is quenched. This mode of growth would show up at a region of the phase diagram depending on the ratio of the substrate to interlayer interaction strengths.<sup>19</sup> Within our resolution, our midlayer features seem to take place at the same coverage at which the  $\sqrt{3} \times \sqrt{3}$  epitaxial phase of He on graphite was observed,<sup>2</sup> and we therefore adopt this model as an explanation of our results. Finally, the epitaxial region in the phase diagram extends to temperature higher than the roughening temperature,<sup>19</sup> 1.08 K, which explains why the 1.3-K isotherm exhibits the high-pressure transitions but not the layering ones, such as seen at 0.1 K.

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