Third-Sound Study of a Layered Superfluid Film

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Isothermal scans of third-sound velocity as a function of ^{4}He coverage on graphite exhibit pronounced dips with integral layer periodicity. The minimum ^{4}He coverage on graphite needed to support third sound is nearly three layers. The heat-capacity isotherm exhibits minima at layer completion but there is no noticeable feature related to the onset of superfluidity. High-resolution adsorption isotherms below 1 K show that ^{4}He film grows layer by layer through at least seven layers.

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Experiments on thin adsorbed ^{4}He films find superfluidity is possible at sufficiently low temperature if the surface coverage n exceeds a critical value, n_0, commonly called the inert layer coverage [1-3]. The nature of the transition at $T=T_c$ is dependent on the topology of the adsorbing surface; on a planar substrate, for example, the transition is describable by the model of Kosterlitz and Thouless (KT) [1,2]. These results were obtained with Mylar, glass, and other substrates with disordered surface potentials. In these systems, the absorbed ^{4}He film does not grow in a layer-by-layer fashion and the surface coverage reported in terms of atomic layers has only a statistical meaning. In contrast, evidence of layer-by-layer growth of ^{4}He on graphite has been found in vapor pressure isotherms down to 1.35 K [4] and third-sound isotherms down to 1 K [5]. It is, however, difficult to deduce definitive superfluid onset behaviors of ^{4}He on graphite in the $T=0$ limit (e.g., n_0) from these experiments [5-7].

In this Letter we report simultaneous vapor pressure isotherm and third-sound measurements of ^{4}He adsorbed on graphite with coverage between two and seven layers down to 0.639 K and a complementary low-temperature heat-capacity study near and above the completion of the third layer. Our experiments show that ^{4}He exhibits layer-by-layer growth on graphite up to at least seven layers and we found the minimum film thickness for superfluidity, or at least what is necessary to support third-sound resonance, to be three (solid) layers. We do not find any heat-capacity feature directly related to the onset of superfluidity in this system.

Figure 1 shows volumetric vapor pressure isotherm results at 0.639 and 1.2 K measured with an *in situ* diaphragm pressure gauge with a sensitivity of 2×10^{-7} Torr. The sample cell contains a third-sound resonator and a piece of graphite foam (0.25 g). The coverage scale is normalized against the completion of the $\sqrt{3}\times\sqrt{3}$ registered phase (areal density is 0.0637 atom/Å^2) of a 74-K N_2 isotherm [8]. Layer-by-layer growth of ^{4}He can clearly be resolved after the completion of the second layer and up to at least the seventh layer. Comparison with the vapor pressure isotherms measured by Polanco and Bretz [4] above 1.35 K shows that layering growth becomes more clearly defined below 1 K.

The prediction of the Frenkel-Halsey-Hill (FHH) equation [5-7,9], including allowance for the dense first two layers, is shown as a dashed line in Fig. 1. The FHH equation states that the film thickness d, measured in Å, can be deduced from

$$d=\left(\frac{T}{\alpha}\ln\frac{P_0}{P}\right)^{-1/3}, \tag{1}$$

where α ($=1900$ K Å^3) is the adsorption coefficient [9] and P/P_0 the reduced pressure relative to saturated vapor pressure P_0. It appears that the FHH model, relied upon by many experiments, underestimates the film thickness by nearly a full layer. The reason for the discrepancy is related to the fact that the FHH model assumes the adsorbed film to be a structureless fluid film and each layer is assigned a statistical thickness of 3.58 Å, consistent

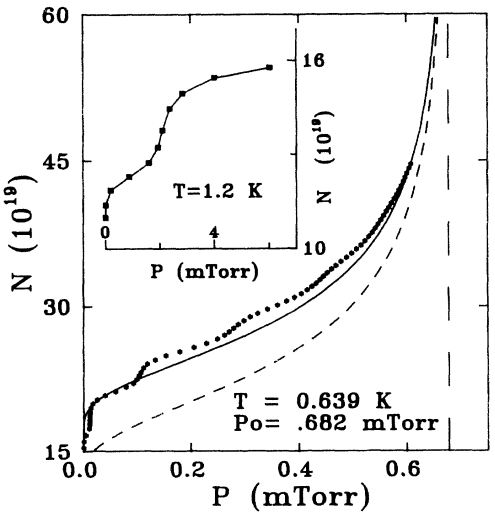

FIG. 1. Inset: Volumetric adsorption isotherms at $T=0.639$ and 1.2 K. The second, third, fourth, fifth, and sixth layers complete respectively at 12×10^{19}, 16.5×10^{19}, 21×10^{19}, 25.5×10^{19}, and 30×10^{19} atoms. The surface area of graphite foam is 5.9 m^2. The dashed line is due to the FHH model, while the solid line represents the result of the pseudosubstrate model discussed in the text.

with bulk liquid density. The actual equivalent densities of the first two layers are respectively about 1.5 and 1.1 times that of bulk liquid (see below) and these two layers are also highly compressed in their vertical separation from the graphite surface. In order to account for the effect of the first two highly compressed layers on the adsorption of subsequent fluid layers, Cheng and Cole [10] modeled a multilayer film of thickness d as two parts. The first two solid layers of thickness D_0 (=4.42 Å) act as a pseudosubstrate for the rest of the film of thickness d'; $d=d'+D_0$. The modified FHH equation then has the form

$$d'=\left[\frac{T}{\gamma(d')}\ln\frac{P_0}{P}\right]^{-1/3}, \tag{2}$$

where

$$\gamma(d')=\gamma^{a\text{-}ps}-\gamma^{a\text{-}a}+(\gamma^{a\text{-}s}-\gamma^{a\text{-}ps})(1+D/d')^{-3}. \tag{3}$$

For the ^{4}He-graphite system, the adsorption parameters have the values [10] $\gamma^{a\text{-}s}=2018$ K Å^3, $\gamma^{a\text{-}a}=116$ K Å^3, and

$$\gamma^{a\text{-}ps}=n_{1+2}\gamma^{a\text{-}a}/\rho_{liq}D_0=246\ \text{K Å}^3.$$

Superscripts a, s, and ps stand for adsorbate (^{4}He), substrate (graphite), and pseudosubstrate, ρ_{liq} is the liquid volume density, and n_{1+2} is the bilayer areal density (see below). The solid line in Fig. 1, showing much better agreement with data, is based on the modified FHH model as shown in Eqs. (2) and (3).

Third-sound measurements were made using the standard resonance method [6]. The resonator is a cleaved leaf of highly oriented pyrolitic graphite (HOPG) cut into an annulus. The third-sound velocity as a function of film coverage at 0.65 and 1.00 K is shown in Fig. 2. For comparison, the 2D isothermal compressibility of the film

$$K_T=\frac{1}{n^2T}\frac{\partial n}{\partial \ln P} \tag{4}$$

deduced from the isotherms in Fig. 1 is also shown. The vertical dashed lines show completion coverages of successive layers occurring at compressibility minima. The second layer completes at 0.204 atom/Å^2; for higher layers the incremental increase in coverage per layer is 0.076 atom/Å^2. These values are in good agreement, within 3%, with the scale proposed by Bretz [11] and with the recent high-precision and extensive heat-capacity study by Greywall and Busch [12] (GB).

The most prominent feature of the third-sound results are the strong dips which occur at integral layer periodicity. Since third-sound velocity is inversely proportional to the compressibility of the film, these dips are found between layer completion coverages [13]. These dips are much more pronounced than the oscillations seen in two earlier third-sound experiments carried out above 1 K [5,6]. For a structureless ^{4}He film on a substrate such as

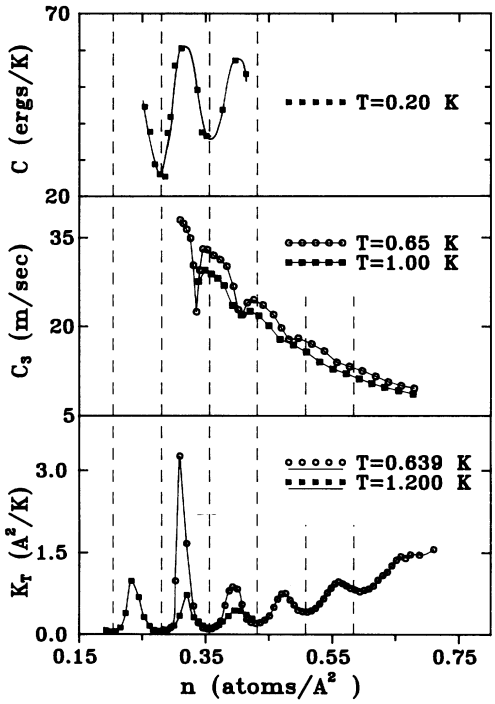

FIG. 2. Heat capacity C, third-sound velocity C_3, and isothermal compressibility K_T of ^{4}He film adsorbed on bare graphite as functions of film areal density. The surface area of the heat-capacity graphite foam sample is 2.19 m^2. The dashed vertical lines indicate completion of successive layers beginning from the second layer.

glass, the inert layer d_0 can and has been obtained from third-sound isotherms via the relation [14]

$$C_3^2=\frac{K_B}{m_4}\frac{\rho_s}{\rho}\left[\frac{3\gamma}{d^4}\right](d-d_0), \tag{5}$$

where ρ and ρ_s are the bulk liquid density and bulk superfluid density, respectively. For temperatures below 1 K, ρ_s/ρ is close to unity.

In view of the success of the modified FHH model for ^{4}He on graphite as shown in Fig. 1, Eq. (5) is modified to the form

$$C_3^2=\frac{K_B}{m_4}\frac{\rho_s}{\rho}\left[\frac{3f(d',D_0)}{d'^4}\right](d'-d_0'), \tag{6}$$

with

$$f(d',D_0)=\gamma^{a\text{-}ps}-\gamma^{a\text{-}a}+(\gamma^{a\text{-}s}-\gamma^{a\text{-}ps})(1+D_0/d')^{-4} \tag{7}$$

and d_0' as the inert layer above the pseudosubstrate.

According to Eq. (6), a plot of $\Gamma\equiv C_3^2(d')^4/f(d',D_0)$ vs d' would yield an intercept as the inert layer (see Fig. 3). The extrapolation of Γ, up to $d'\sim 12$ Å and at coverages away from the dips, shows a $d_0'=3.2\pm0.6$ Å which is equivalent to $n_0'=0.068\pm0.013$ atom/Å^2. Together with the two-layer pseudosubstrate, our data suggest a total

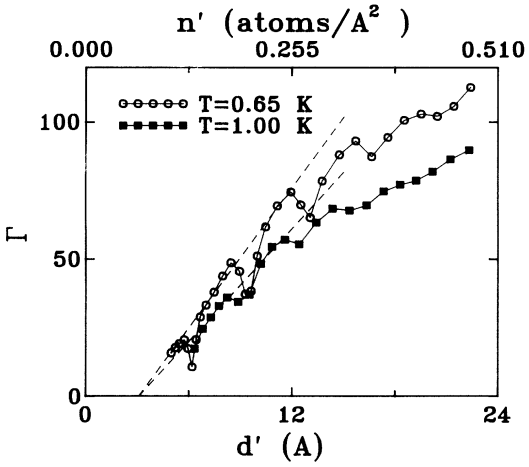

FIG. 3. Analysis of third-sound data to determine the inert layer coverage. Γ is defined in text. Linear extrapolations of the data below $d'=12$ Å yield a value $d_0'=3.2\pm0.6$ Å. For the drop of Γ above 12 Å see the discussion in the text.

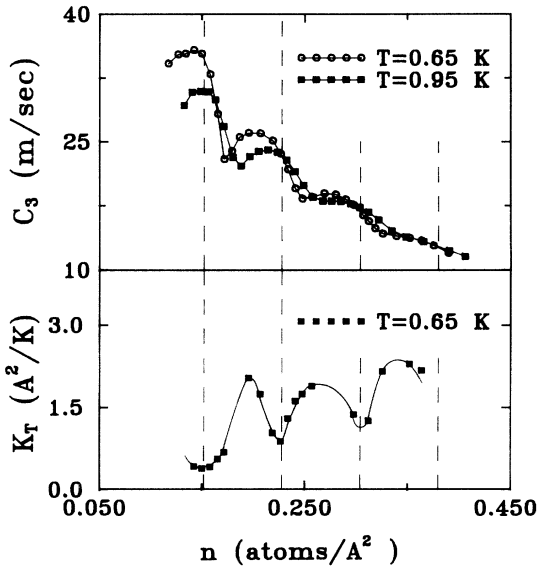

FIG. 4. Third-sound velocity C_3 and isothermal compressibility K_T of ^{4}He film adsorbed on graphite preplated with two layers of H_2 as a function of n. The dashed vertical lines indicate completion of successive layers beginning with the second layer.

inert film thickness very close to three layers. Since Eqs. (5) and (6) are derived assuming a structureless film, it is reasonable to use velocity values corresponding only to layer completion condition, that is, away from the dips. Above seven layers, Γ drops substantially below the values based on linear extrapolation from small d'. We do not know the reason for this. Retardation effects, which are important for thick films [9], can only account for about 30% of the discrepancy found at the completion of the seventh layer. It appears that Eq. (5), which works well for glass substrates [14], may not be easily modified as we have done for a layered superfluid film. Torsional oscillator measurements of ρ_s, whose interpretation is less model dependent, should be particularly revealing.

Recent inelastic neutron-scattering measurements [15] appear to be consistent with our finding of an inert film thickness equal to three layers. Our third-sound isotherms indicate that the onset film thickness at 0.639 K lies between 3.4 and 3.45 layers ($d=3.4$ and 3.45 layers correspond to when there is a hint and when there is a fully developed third-sound resonance, respectively) and at 1 K between 3.69 and 3.77 layers. The onset film thicknesses at 0.65 and 1.00 K, deduced from the KT relation assuming superfluidity begins at three layers at $T=0$, are 3.43 and 3.67 layers, respectively. This is consistent with the result of our extrapolation shown in Fig. 3.

The incremental areal density of the third layer at 0.076 atom/Å^2 is identical to that of upper layers and scales with the volume density of bulk liquid. If the third layer is liquidlike in the $T=0$ limit, then an obvious question is why it does not exhibit superfluidity or support third-sound resonance. Heat-capacity results of GB, however, indicate that the third layer of ^{4}He on graphite or the three-layer film at its completion is solidlike [12].

We have also measured the heat capacity of ^{4}He on graphite down to 0.1 K at coverages near and above the completion of the third layer with an ac technique. Our result is summarized as a 0.2-K isotherm in Fig. 2. As in GB, minima in C are found at the completion of the third and fourth layers. Our C vs T scans, as well as those of GB, do not show any signature that can be identified as that related to the KT superfluid transition at coverages above three layers. There is as yet no firm experimental evidence for the broad heat-capacity maximum [1] predicted above the transition temperature T_c in the 2D thin-film limit, i.e., with T_c below 1 K. It is not clear whether the absence of such a heat-capacity signature is common for all planar superfluid films or is unique for films adsorbed on a periodic substrate such as graphite. This absence of any thermodynamic signature contrasts sharply with the findings of thin ^{4}He films in Vycor. In the Vycor case, C vs T scans are characterized by a small but sharp peak at T_c. Low-temperature C vs n isotherms, possibly reflecting the effect of a random surface potential, show a prominent maximum separating the superfluid and nonsuperfluid regions [3].

We repeated the simultaneous third-sound and vapor pressure isotherm measurements after preplating the graphite surface with exactly two layers of H_2. The coverage of the H_2 film was determined via an isotherm at $T=12$ K which clearly showed a step due to the condensation of the second layer. Some of the third-sound and compressibility results are presented in Fig. 4. Vertical dashed lines due to compressibility results indicate completion of successive layers: The second layer completes

at 0.155 atom/Å^2 and the higher layers have a density of 0.076 atom/Å^2. The third-sound velocity again shows dips with an integral layer periodicity as on bare graphite. Third-sound resonances at 0.65 and 0.95 K are first observed at film thicknesses between 1.49 and 1.54 layers and 1.68 and 1.75 layers, respectively. When this is compared with the results on bare graphite, the minimum film thickness for superfluidity of ^{4}He on graphite coated with two H_2 layers is found to be close to one layer.

Shirron and Mochel [16] (SM) have recently reported similar dips in the third-sound velocity of superfluid ^{4}He films adsorbed on a ten-layer-thick H_2 film, but with a periodicity close to half a layer. We do not understand this discrepancy. It is possible that third sound behaves differently on thick and thin H_2 films. It is also possible that the calculated surface area of H_2 (via Brunauer-Emmett-Teller fits of pressure isotherms) in SM is incorrect because of nonuniform H_2 deposition and/or incorrect parameters.

To conclude, we found ^{4}He films grow layer by layer on graphite. The minimum film thickness of ^{4}He on bare graphite necessary to detect third-sound resonance is deduced to be close to three (solid) layers. No heat-capacity signature is found at superfluid onset. When graphite is coated with two H_2 layers, the superfluid onset coverage is reduced by nearly two layers. In both cases, third-sound velocity shows pronounced dips with integral layer periodicity.

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