Heat Capacity of Fluid Monolayers of ⁴He

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The heat capacity of ⁴He adsorbed on graphite has been precisely measured over a fine grid of coverages for temperatures extending down to 100 mK and for coverages up to five atomic layers. The data indicate that the two-dimensional liquid is self-bound in each of the first three layers with an areal density of about 0.04 atom/Å². There is also evidence suggesting that this liquid undergoes a Kosterlitz-Thouless transition.

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The submonolayer phase diagrams of 3 He and 4 He adsorbed on graphite appear remarkably similar [1] for areal densities greater than that corresponding to the $\sqrt{3}$ registered phase R. At lower coverages, however, the generally accepted ⁴He diagram [1-3] differs substantially from that recently proposed [4,5] for ³He. Here ³He heat-capacity data [4] indicate that this system exists as a two-dimensional (2D) fluid F, down to presumably absolute zero, although there is evidence suggesting some type of phase transition near 3 mK. In contrast, low-coverage heat-capacity data for ⁴He exhibit a rounded maximum near 1 K which has been ascribed to many different phenomena [6]. At present, the consensus appears to be that this "peak" corresponds to the crossing of a phase boundary separating 2D vapor at high temperature and a vapor condensed-phase coexistence region at lower temperature. Although this condensed phase was once thought to be the 2D liquid state [7,8], it is now usually taken to be the R phase; see Fig. 1(a) [9]. The low-coverage 4 He system at temperatures less than 1 K is thus expected to be in a two-phase region bounded by the pure 2D gas phase near zero coverage and by the pure R phase at ρ_R (0.0637 atom/Å²) even though there is no convincing evidence from either scattering or thermodynamic experiments to substantiate this belief. However, given the quantitative similarities between the ³He and ⁴He phase diagrams in the vicinity of the registered phase, the recent heatcapacity results for ³He raise several questions and doubts about the interpretation of the ⁴He phase diagram. The very-low-temperature ³He data show unambiguously that this system enters into a two-phase region only near ρ_R and that the broad portion of the phase diagram associated with the registered phase is actually an F-R coexistence region. In the ⁴He picture the corresponding region of the phase diagram is thought to be the registered phase existing with as much as 30% vacancies [2].

In this Letter we present new low-temperature heatcapacity data for ⁴He/graphite which contradict the current view and indicate a two-phase region involving the *R* phase which is restricted, as for submonolayer ³He, to $0.04 \leq \rho \leq \rho_R$; see Fig. 1(b). At lower coverages there is a coexistence of the 2D gas and the liquid which is believed to be superfluid. We also have evidence at much higher coverages suggesting that each of the next several atomic layers undergoes a similar evolution with increasing layer density. The new results are based on precise heat-capacity measurements which extend to lower temperatures and higher coverages than in previous experiments and also cover a finer grid of coverages. In the regions of overlap the new data are generally consistent with earlier results.

The measurements were made using the adiabatic heat-pulse technique for temperatures between 0.1 and 3.5 K and for coverages extending up to 0.45 atom/Å² $(\sim 5 \text{ layers})$. The calorimeter was a thin-walled silver cell which contained 14.2 g of graphite in the form of 0.13-mm-thick sheets of Grafoil bonded onto both sides of many pieces of 0.025-mm-thick silver foil. These foils were thermally attached to the base of the cell along with the heater and thermometer. Each of the 84 samples was obtained by making precise incremental additions to the amount of ⁴He in the cell via a small filling capillary. These samples were annealed at an elevated temperature (15 K for the lowest-coverage samples) for several hours and then cooled over a period of 12 to 18 h to the starting temperature of 90 mK. The coverage scale was normalized in the usual manner by taking the coverage corresponding to the largest $\sqrt{3}$ registered phase heat-capacity



FIG. 1. Comparison of phase diagrams proposed for ⁴He adsorbed on graphite. (a) Phase diagram due to Schick, Ref. [9]. (b) Phase diagram determined in the present work. The *G-L* coexistence boundary is schematic.

peak to be 0.0637 atom/Å². This implied a total substrate surface area of 261 m². All of the data were corrected for the addendum contribution. Above monolayer completion a correction was also applied for desorption effects.

Figures 2(a)-2(e) show the heat-capacity results plotted versus coverage for several fixed temperatures between 0.1 and 2 K. The points plotted were obtained from spline fits passing through each of the measured data points obtained as a function of temperature at fixed density. The smooth curves in Fig. 2(f) show the location of heat-capacity peaks which help to define various regions in the temperature-coverage phase diagram. The rather sharp maximum in Fig. 2(f) near $\rho = 0.06$ corresponds to the order-disorder transition of the commensurate solid, while the solid curve above roughly 0.08 shows the location of melting peaks for the first-layer incommensurate solid. By analogy with the first-layer phase



FIG. 2. Heat capacity as a function of coverage for several isotherms. The top panel shows smoothed results for the locations of peaks in the heat capacity.

diagram, the region near $\rho = 0.20$ is associated with a second-layer registered phase and the higher density region with the second-layer incommensurate solid phase. Note that this second-layer solid continues to melt at 2 K even when covered by several additional layers.

The oscillations in the low-temperature isotherms of Fig. 2 indicate the formation of successive atomic layers. A rapid increase in heat capacity occurs each time the first atoms are promoted into the next level since these atoms constitute a nearly ideal gas with a very low degeneracy temperature and make a classical contribution to the total heat capacity. Promotion into the second, third, fourth, fifth, and sixth layers is therefore located at total coverages of 0.120, 0.212, 0.288, 0.364, and 0.440 atom/ $Å^2$, respectively. For the higher layers the incremental increase in coverage is 0.076 atom/Å². Assuming a triangular lattice, this corresponds to a near-neighbor spacing of 3.90 Å which is only 3% smaller than that computed for bulk liquid under saturated vapor pressure taking a close packing of atoms. We note that our coverage for third-layer promotion at low temperatures is significantly higher than that determined by Bretz [10] and others using vapor pressure and heat-capacity isotherms measured above 1 or 2 K. Our highest-temperature uncorrected data also increased rather sharply prior to lowtemperature third-layer promotion. This is implied in Fig. 3 where we show the heat of adsorption obtained from fits of our heat-capacity data above 1 K by an exponential expression. The decrease in q at $\rho \approx 0.18$ may correspond to the second layer resisting the loss of registry at high temperature by promoting atoms into the third level.

Focusing now on the first adsorbed layer, if the coverage region below ρ_R corresponds to a single two-phase region, as has been proposed, then the isotherms below roughly 1 K should be linear functions of ρ over nearly the entire range. Figures 2(a)-2(d) show that this is not the case. First of all, near $\rho = 0.06$ each of the isotherms shows a change in behavior similar to that recently reported [5] for adsorbed ³He. It was then suggested that this was due either to zero-point vacancies or to the finite size of the homogeneous regions. Assuming this is true also for ⁴He and ignoring the region between 0.06 and ρ_R , the isotherms show an accurate linear dependence only above roughly 0.04. Note that placing a zerotemperature phase boundary at $\rho = 0.04$ also determines a



FIG. 3. Heat of adsorption determined from fits of the higher-temperature heat-capacity data.

natural extension for the high-temperature phase boundary mapped out by the melting peaks of the R phase, Fig. 2(f). This enclosed region of the diagram associated with the R phase is analogous to the F-R coexistence region determined for adsorbed ³He. In the case of ³He the low-temperature boundary could be located precisely at 0.043 because of the large difference between the lowtemperature heat capacities of the Fermi fluid and the registered solid. A somewhat smaller coverage for the ⁴He boundary, relative to ³He, would be consistent with the stronger binding to the graphite substrate. An F-Rcoexistence above 0.04 is also suggested by the fact that the 1-K maxima observed at lower coverages, and presumably directly associated with the fluid phases, continue to exist above 0.04, but suddenly decrease linearly towards zero amplitude at $\rho = \rho_R$ while showing no detectable shift in temperature. Other important evidence is provided by the second-layer results discussed below. These data suggest a phase diagram completely analogous to that of the first layer, but show more clearly defined two-phase regions.

One possibility for the region below $\rho = 0.04$ is a pure fluid phase extending to zero temperature, as for adsorbed ³He. The rounded peaks in c vs T for ⁴He might then be associated with a Kosterlitz-Thouless [11] (KT) transition in the Bose gas. A difficulty arises, however, because T_c should be nearly proportional to the areal density, but the observed peak position varies by less than 50% over a fourfold increase in density and also does not extrapolate to zero temperature at zero coverage. In the KT theory the heat capacity has only an unobservable essential singularity at T_c . The maximum which appears at a somewhat higher temperature due to the increasing number of unbound vortices is nonuniversal; however, $T_{\rm max}$ is expected [12] to be roughly proportional to T_c and should therefore have a very similar coverage dependence.

A peak position which changes very little with coverage could be quite naturally explained by a gas-liquid, G-L, coexistence. And, indeed, it has been determined theoretically [13,14] that the 2D liquid phase of ⁴He is self-bound with a density of about 0.04 atom/Å².

Because the phonons are the only excitations in the liquid at sufficiently low temperature, the heat capacity should be proportional to T^2 in this regime. The lower right-hand panel in Fig. 4 shows our first-layer data at a comparable coverage plotted on logarithmic scales to demonstrate consistency with this temperature dependence. The amplitude of this contribution implies a Debye temperature of 5.1 K which agrees well with the theoretical value [14], 4.9 K.

Ceperley and Pollock [15] have studied the 2D ⁴He system using computational path-integral methods and have determined the heat capacity at a density of 0.0432. These results, which show a KT maximum, are compared with our first-layer data in the lower left-hand panel of Fig. 4. The agreement in temperature location, ampli-



FIG. 4. Heat capacity of the first-, second-, and third-layer fluids. The dashed curve shows the calculations of Ceperley and Pollock (Ref. [15]) at a density of 0.0432 atom/Å². The peak in the third-layer data near 2 K is due to the melting of the second-layer solid.

tude, and peak width is additional evidence that we do have a fluid at this coverage and that this fluid is undergoing a KT transition.

The fact that the low-temperature isotherms do not show an extended region linear in ρ below $\rho = 0.04$ might be explained by surface heterogeneity being important at low coverages or by the shrinking size of the liquid regions at low coverage affecting details of the 2D superfluid phase. This latter effect is also suggested by the finding that T_{max} is not entirely independent of coverage. The fact that the second-layer isotherms show more well-defined two-phase regions may be due to the smoothing of the surface by the first layer.

A puzzling aspect of the data in the G-L regime is that only a single feature is present in the heat capacity as a function of temperature. One might have expected two features: a discontinuity corresponding to the crossing of the phase boundary separating the two-phase and purephase regions, and at a different temperature the KT peak.

It seems difficult to argue that the single feature observed is not the KT maximum but simply the discontinuity rounded by substrate heterogeneity and thermal excitations in the liquid state [8]. This is not only because of the fine agreement with the theoretical calculations, but also because the peak amplitude should then be quite sensitive to the particular graphite substrate used, and yet all experiments give essentially the same results. Moreover, it would then be difficult to explain the persistence of these maxima into the region above $\rho = 0.04$. On the other hand, it would be equally difficult to understand the complete absence of the discontinuity. At the lower areal densities, one possible explanation is that there is only a single transition in this 2D quantum system with vaporization and vortex unbinding occurring simultaneously. The problem remains at densities near the upper end of the *G-L* region, because here the dense fluid phase should undergo a KT transition at temperatures greater than the phase separation curve. It is for these reasons that the *G-L* phase boundary in Fig. 1(b) is only schematic.

The second-layer system evolves in a manner completely analogous to that of the first layer. At low secondlayer coverages there is a peak in the heat capacity, Fig. 4, with a temperature location nearly independent of the coverage; see Fig. 2(f). At higher coverages a second peak emerges at a higher temperature and over a small coverage range develops into the sole feature. This peak is then suddenly replaced by a much sharper peak which appears now at a lower temperature. By comparison with the first-layer results the high-temperature (1.5 K) feature is associated with some type of commensurate solid.

Figure 2(a) is thus interpreted as indicating an F-R coexistence region in the second layer for $0.16 \le \rho \le 0.19$ ($0.04 \le \rho_2 \le 0.07$) and also a well-defined G-L coexistence region at lower second-layer coverages. The heat-capacity-versus-temperature results in the fluid regime, Fig. 4, exhibit a maximum with about the same amplitude as observed for the first layer. The peak is now, however, sharper and located at a lower temperature [8]. The changes relative to the first-layer results are attributed to the weaker substrate binding which leads to greater out-of-plane motion and an altered effective atom-atom interaction [16].

It should be noted that our interpretation of the second-layer data differs considerably from the conclusions reached by Polanco and Bretz [8], who made measurements on fewer samples and only above 0.4 K. They determined that the second layer does not form any registered structures nor does it solidify until compressed by further layers.

Our third-layer data also yield isotherms which exhibit a G-L coexistence region and a fluid heat capacity which is extremely similar to that of the second layer, Fig. 4. The peak in Fig. 4 near 2 K is due to the melting of the second-layer solid. It is not clear if the rapid decrease in the third-layer isotherms near $\rho_3 \approx 0.04$ is due to solidification of this layer or merely indicates the compression of the third-layer fluid.

The isotherms for the fourth and fifth layers differ from those of the underlying layers and do not show any extended region linear in ρ which could be identified as *G-L* coexistence. This suggests that the liquid phases in the higher layers may not be self-bound.

With increasing temperature the oscillations in the isotherms attenuate progressively more rapidly as a function of coverage. At 0.7 K there is evidence for the existence of only four distinguishable layers. At 2 K the signature for the fourth layer has also disappeared, but is replaced by an onset for a rapid increase in the heat capacity corresponding to the initial development of the lambda peak of bulk ⁴He. Since the feature in the 2-K isotherm located just prior to fourth-layer promotion corresponds to the second-layer melting peak moving above 2 K, the first two layers are solid when atoms are promoted into the fourth layer and are not involved in the development of the transition. The third layer is presumably a fluid at 2 K, implying that the adsorbed ⁴He system is already moving toward the bulklike behavior beginning with two fluid layers.

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