# Heat Capacity of Multilayer $He^4$ on Graphite*

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Helium films are explored in the temperature range 1–2.8 K for thicknesses of 3–11 atomic layers. Sharp heat-capacity peaks for the thinnest films appear to indicate melting of the second-layer solid. Thicker films display coverage-dependent truncations of the λ-point specific-heat anomaly, and cell thermal conductivity shows abrupt changes near these truncation points. Comparison with mass-flow measurements leads to the discussion of a possible intermediate superfluid phase.

Liquid helium in a finite geometry displays properties considerably different from those of bulk. In particular, as the film thickness is reduced on substrates of rouge,[1] Vycor glass,[2] and $TiO_2$,[3] the λ-point specific-heat anomaly rounds, is suppressed in $T$, and finally disappears at a few layers. Film-transport studies[4] find that upon reducing the thickness, the onset temperature of superfluidity decreases more rapidly than the heat-capacity anomaly and becomes dissociated from it.[5] Experiments have been extended down to partial monolayer helium films, where it has recently become apparent that substrate heterogeneity critically affects the film properties.[6] But do the first few layers effectively smooth any surface heterogeneity so that the upper layers remain undisturbed? Or, instead, do substrate properties continue to affect distant layers? Recent evidence for the latter possibility[7,8] is strengthened by the observation of multilayer heat capacities considerably more structured than those found in previous experiments. A second-layer melting transition is detected and distinct heat-capacity structure is seen near the temperature of superfluid onset in highly unsaturated helium films.

The graphite-filled calorimeter and technique used here have been described previously.[6] A $He^4$ vapor-pressure isotherm at 4.2 K indicates monolayer completion at $N = 96$ cm$^3$ STP. At 96–98 cm$^3$ and near 165 cm$^3$, 1–3-K heat-capacity isotherms show abrupt increases in heat capacity, signaling first- and second-layer completion. These agree with a 2-K pressure isotherm, indicating second-layer completion at about 165 cm$^3$. The 2-K isotherm is described well for $n > 2$ by a Frenkel-Halsey-Hill formula,[9] $\ln(P/P_0) = -\alpha/n^3$, where $P_0$ is the saturated vapor pressure and $\alpha$ is a constant, if each layer has a capacity of 65 cm$^3$. Film coverage is given henceforth in terms of $n$, the total thickness in completed atomic layers, with $n = 1$ defined as 96.5 cm$^3$, and $n = 2$ as 164.5 cm$^3$. We emphasize that all coverages are given assuming complete adsorption and that appreciable layer promotion and film depletion occurs at finite $T$. Excess heat capacity due to desorption is subtracted out according to a thermodynamic relation between pressure and desorption heat capacity.[10] Also, subtracted from all films are the empty calorimeter signals and the heat capacity for $n = 1$. The monolayer is known to be compressible[11] and an observed shift of the melting peak from 7.38 K for the complete, but bare, monolayer to 8.62 K in the presence of a partial second layer reflects an increase in monolayer density. But the continued presence of the monolayer solid when further layers are added gives credibility to the $n = 1$ subtraction (which is small).

Second-layer signals are two-dimensional classical gaslike and in general lack the richness of the monolayer films. They do, however, provide important comparisons with the monolayer and these are discussed elsewhere.[12] Heat-capacity results when a partial third layer is adsorbed are shown in Fig. 1. The signal for $n = 2.09$ is gaslike, but by $n = 2.19$ a peak has appeared which rises in $T$ and sharpens considerably as coverage approaches $n = 3.0$. For higher coverage the peak broadens again and continues to increase in $T$. Since Fig. 1 closely resembles the monolayer melting peaks of Bretz, Huff, and Dash,[13] it is natural to ask if the peaks of Fig. 1 might not represent solidification now occuring in the second layer.

With about a 5% density increase of the completed second layer (assuming 12.7 Å$^2$/atom at a complete layer and the same substrate area for first- and second-layer adsorption) the peaks of Fig. 1 lie on the melting line of Ref. 10. Like the monolayer, the second layer is undoubtedly highly compressible and the presence of a third

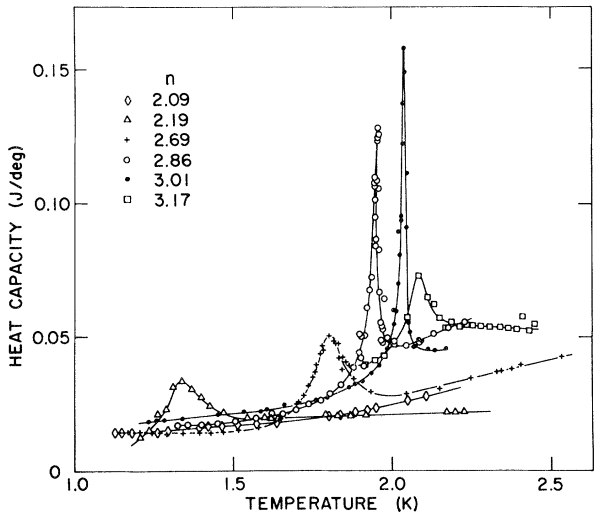


FIG. 1. Reduced-heat-capacity data for coverages up to the filled third monolayer. Solid lines have been added to guide the eye.

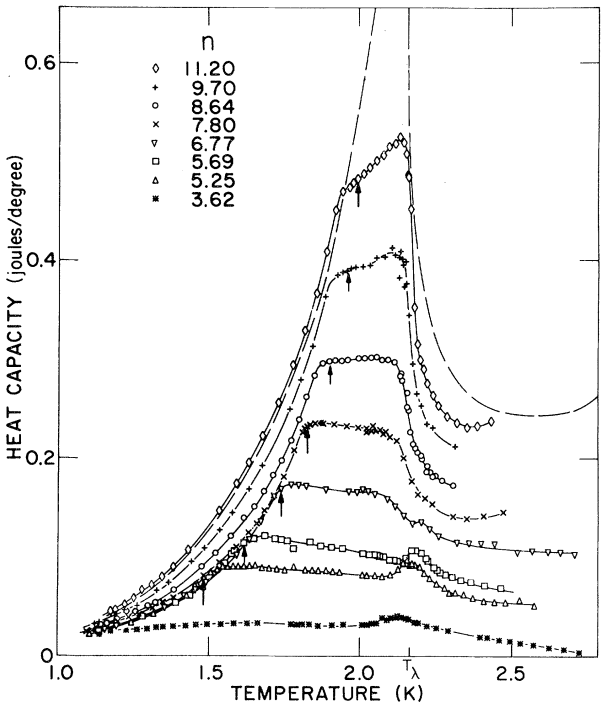


FIG. 2. Reduced heat capacity of multilayer films. Dashed line, heat capacity expected if all atoms above the second solid layer for the film $n = 11.20$ behaved as bulk. Arrows indicate temperature below which cell relaxation times are immeasurably small. Solid lines are drawn to guide the eye.

adsorbed layer could increase the density of the second enough to induce solidification. In addition to lateral compression, the third layer might assist second layer solidification by causing a vertical compression, making the second layer more nearly two dimensional and thereby increasing the steric hindrance between atoms. A $T^2$ dependence of the heat capacity is not observed, but rather, the signal remains large at the lowest $T$'s. This is interpreted as arising from a quasi gaslike contribution of the partial third layer. Although it is not understood why the peak broadens again for $n = 3.17$, it is probably not a coincidence that the sharpest peak observed at $n = 3.01$ occurs just at layer completion.

Figure 2 gives the reduced heat capacities of multilayer films for $3.62 \leq n \leq 11.20$. For the thinnest films second-layer melting peaks are visible near $T_\lambda$. The slight increase in $T$ of these peaks with coverage is in agreement with the compressibility arguments just presented. The dashed line in Fig. 2 gives the heat capacity expected for 9.2 layers of bulk liquid.[14,15] Below about 1.9 K this curve corresponds closely to the film at $n = 11.2$. Then, assuming a negligible low-$T$ heat-capacity contribution of the second layer (only the first layer was subtracted in Fig. 2) the heat capacity of the $n = 11.2$ film appears bulklike. But above 1.94 K, a temperature which we shall designate $T_p(11.2)$, a distinct truncation of the $\lambda$ anomaly occurs. Thinner films likewise correspond to bulk values at low $T$ and display thickness-dependent peak truncations above temperatures defined as $T_p(n)$. These plateaus above $T_p$ extend almost to $T_\lambda$(bulk) for all films of Fig. 2.

The truncation of the bulk $\lambda$-point anomaly can be viewed differently by plotting the incremental specific heat $\Delta c/\Delta N k$ for adjacent coverages. In this way attention can be focused on the heat-capacity contribution of $\Delta N$ atoms which are added to the film. Representative $\Delta c/\Delta N k$ curves are shown in Fig. 3, with the bulk specific-heat anomaly provided for comparison. We immediately observe that at the highest coverage, curve 1, the incremental heat capacity has a peak resembling that of the bulk liquid rather than a truncation. This peak rises almost twice as high up the bulk $\lambda$ curve as does $n = 11.20$ of Fig. 2. The plateau of Fig. 2 appears as a shoulder on the rounded $\lambda$ anomaly in Fig. 3, possibly reflecting alterations in the heat capacity of the deeper layers. As coverage is reduced (curve 2) further rounding of the peak occurs while the

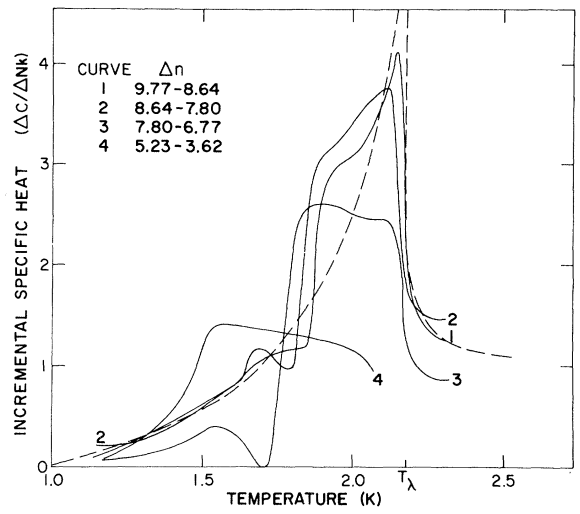


FIG. 3. Incremental specific heat $\Delta c/\Delta N k$, where $k$ is Boltzmann's constant. These curves are obtained by subtracting smooth fits for adjacent films of Fig. 2. Dashed line, bulk specific heat.

shoulder remains strong to form the plateau of curve 3. This feature now dominates to the thinnest films (curve 4). Notice that all curves tend toward the bulk at both the lowest and highest $T$'s shown, and possess an abrupt fall at $T_\lambda$(bulk). (Curve 4 is not shown near $T_\lambda$ since the second-layer melting peaks disrupt the differential signal.)

The film thermal conductivity $\kappa$, roughly proportional to the measured heat capacity over calorimeter relaxation time $\tau$, is found to vary dramatically with coverage and temperature. The arrows in Fig. 2 indicate the $T$ for each sample below which $\kappa$ is too large to measure. Within 0.05 K above those arrows $\kappa$ falls abruptly to a small background value ($\tau$ varies from $\lesssim \frac{1}{2}$ sec to 1–2 min in this temperature interval). Recently, Herb and Dash[7] studied mass transport of $He^4$ on graphite surfaces, and observed sudden changes in flow rate of two different types ("onset $A$" and "onset $B$" of Ref. 7) occurring at definite temperatures and thicknesses. I find that the anomalous changes in $\kappa$ of the present study are closely correlated with the mass-flow onset $B$, but occur about 0.05 K lower. Onset $A$ is observed at $T_\lambda$(bulk) for $2.1 \lesssim n \lesssim 2.7$ although the thermal conductivity for the films given in Fig. 1 remains at background everywhere.

The heat-capacity results presented here are markedly different from earlier experiments on other substrates so it must be concluded that somehow surface heterogeneity of geometry plays a greater role in determining the character of multilayer films than previously suspected. One can imagine that the low-$T$ truncation points at $T_p$ can be blurred for films of mixed thickness giving the appearance of a broad maximum which is suppressed in $T$ as the film becomes thinner.

Individual layers above the solid must not behave independently but in consort, for no multiple heat-capacity steps are apparent at $T$'s below $T_p$ in Fig. 2. There is but a single plateau at each coverage. An attractive explanation of peak truncation is that the coherence length in an ordered state is restricted by the finite thickness of the film, preventing further growth of the heat-capacity anomaly.[16] However, coherence-length arguments are thought to permit only gentle changes unlike the abrupt cutoffs at $T_p$ in Fig. 2. An alternative interpretation might be that the plateau between $T_p$ and $T_\lambda$(bulk) reflects some distinct region intermediate between normal and superfluid helium. In fact, the possibility of a region of superfluidity without superflow (having zero critical velocity) in thin helium films has already received considerable attention.[17,18] But the mass flow and $\kappa$ onsets just discussed are found *within* the coverage and $T$ range of the observed heat-capacity plateaus. It appears that the intermediate region corresponds not to superfluidity without superflow, but rather to unstable superflow which has, as $T$ rises above $T_p$, increasing difficulty in propagating over macroscopic distances. Mass flow onsets $B$ are found at slightly higher $T$'s than for thermal onsets at corresponding coverages because mass flow is simply more sensitive and so one can observe signals to higher $T$'s in this intermediate region. Third sound and persistent currents, when measured on graphite, might also find onset temperatures versus coverage which are specified by technique sensitivity.[19]

The superfluid onset temperature for bulk helium is pressure sensitive, yet surprisingly, the rapid fall seen in Fig. 3 occurs near $T_\lambda$(bulk), independent of film thickness. Indeed, a mass-flow onset occurs at $T_\lambda$(bulk) for $n \sim 2.1$, a film which is known to be highly compressed since we have seen that solidification occurs at a slightly reduced temperature![20] This constant $T_\lambda$ might be fundamentally related to the recent observation that $T_c$ for a well-ordered ultrathin superconducting film is only weakly thickness dependent, even down to ~30 Å.[21]

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# Theory of the Critical Temperature of Superfluid Phase Transitions in Two Dimensions*

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An argument is given that a model field theory with an $n$-component order parameter has a nonzero critical temperature for large $n$ in two dimensions. A simple dependence of the depression of the $\lambda$ point below $T_\lambda$(bulk) on film thickness is found which correlates with properties of the heat capacity for multilayer He films on graphite observed by Bretz.

In a very beautiful series of experiments, Bretz[1] has found that the heat capacity of multilayer $He^4$ films (3-11 monolayers) on crystalline graphite exhibits a remarkable modification of the bulk $\lambda$-point behavior. In this Letter it is suggested that the "cutoff $\lambda$-point" behavior observed by Bretz is actually characteristic of a true two-dimensional (2D) thermodynamic phase phase transition of superfluid He. This suggestion is based on a theoretical argument for the existence of a critical temperature $T_c(n)$ for a Ginzburg-Landau (GL) model field theory in two dimensions with an $n \gg 1$. Extension of the argument to films of finite thickness $\nu$ [expressed in units of a zero-temper-