Two-Dimensional Pressure of ^{4}He Monolayers: First-Order Melting of the Incommensurate Solid

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The melting of incommensurate solid ^{4}He monolayers on graphite is studied with a strain gauge sensitive to two-dimensional pressure. The observations are characteristic of first-order transitions broadened by substrate heterogeneity and inconsistent with the calculated behavior of dislocation-mediated melting. These results and other recent experiments raise serious questions as to the completeness of the theory.

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The theory of dislocation-mediated melting of two-dimensional matter and incommensurate solid monolayers predicts the possibility of a continuous transition to an orientationally ordered fluid.[1] Some computer simulations of adsorbed molecular films have been interpreted as support for the theory,[2] but others indicate first-order melting.[3] Experimental transitions in several adsorbed systems are first order,[4] but may be continuous in Xe,[5] Kr,[6] and He[7] on graphite over portions of their phase diagrams. He monolayers are especially suitable for tests of the theory, since their incommensurate solid phases exist over a wide range of density and temperature, with negligible densities in upper layers and vapor, thus satisfying the theoretical conditions for two-dimensional (2D) floating solids. He films were among the first adsorbed systems to indicate continuous melting, which later work has appeared to confirm. However, a recent calorimetric study[8] has raised the possibility that the transitions are intrinsically abrupt, but experimentally rounded by substrate heterogeneity. Calorimetry is especially sensitive to heterogeneity due to entropy effects,[8] but other thermodynamic quantities such as two-dimensional pressure ϕ are less so. The measurements reported here place more precise constraints on the order of the transition than was possible with the specific-heat results.

The temperature dependences of ϕ and the heat capacity give clear distinctions between first-order and continuous melting in ideal (i.e., uniform) films.[9] Their behavior in first-order melting at constant density n is illustrated in Fig. 1; in contrast, dislocation-mediated melting is predicted to produce curves with no sharp features. The shape of $(\partial\phi/\partial T)_n$ evidently resembles the heat capacity in first-order melting. This similarity, which we employ subsequently in the analysis, also holds in continuous melting. In both types of transition the principal density dependence of thermodynamic properties near melting enters through the variation of T_m with n. We may then express the free energy $F(n,T)$ near the transition as a composite of a melting term $F_m(T/T_m(n))$ and a slowly varying background F'. Thermodynamics then yields

$$\left(\frac{\partial\phi}{\partial T}\right)_n=\left(\frac{\partial\phi'}{\partial T}\right)_n+\frac{n}{AT_m}\left[S_m+T\left(\frac{\partial S_m}{\partial T}\right)_n\right]\left(\frac{dT_m}{dn}\right),$$

where S_m and $T(\partial S_m/\partial T)_n$ are the entropy and the constant-density heat-capacity contributions due to F_m, and A is substrate area.

The experiment was performed with a surface strain gauge which permits direct measurement of ϕ. Earlier versions of the device and its operating principles have been described previously[10] in connection with studies of heavier molecules at higher temperatures. Briefly, the gauges detect dimen-

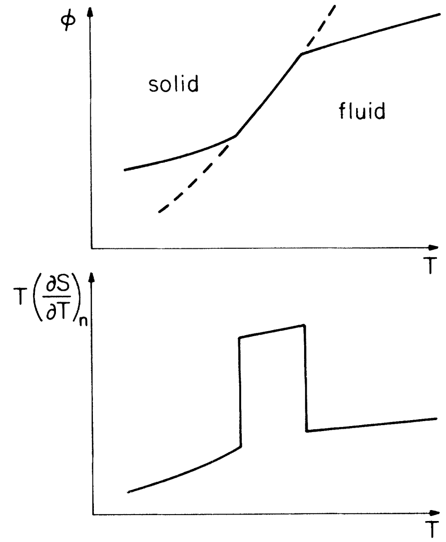

FIG. 1. Two-dimensional pressure ϕ and heat capacity $T(\partial S/\partial T)_n$ of a constant-density monolayer film, in a first-order melting transition.

sional changes of a substrate caused by adsorption, the changes being measured capacitively. The present device is more sensitive than its predecessors. Its form is a cylindrical capacitor, the inner member consisting of a stack of MAT[11] (low-density, compressed, exfoliated graphite) disks, with graphite basal planes preferentially oriented perpendicular to the cylinder axis. The outer (inert) cylinder is a quartz tube with a conducting film on its inner surface. Inner and outer cylinders were ground to provide a 12-μm radial gap on a mean 1.12-cm radius. The capacitor is mounted in a temperature-controlled heavy-walled copper cell thermally attached to a cryogenic liquid reservoir within a vacuum chamber. Film density is controlled and vapor pressure monitored via an external gas-handling system. Details of construction and measurement are given elsewhere.[12]

Capacitance was measured with a low-frequency ac bridge and associated low-noise circuitry; capacitance C_0 in vacuum is 2800 pF at liquid-helium temperatures. Under optimum conditions we could detect changes of 2×10^{-3} pF, equivalent to 0.1-Å dilation of the graphite cylinder radius, but in a typical 24 h run the long-term drift reduced the reproducible sensitivity by about a factor of 3. ϕ is related to C_0 and the capacitance C with adsorbed film, though a gauge constant α, by[10] $\alpha\phi=(C_0^{-1}-C^{-1})$. α was determined by comparing capacitance changes with vapor pressures of He, Kr, and methane over convenient ranges of P and T, via the relation $(\partial\phi/\partial P)_T=n/\rho$ between n and the three-dimensional density ρ of vapor.[9] Repeated He calibrations gave $\alpha=(5.4\pm0.6)\times10^{-7}$ cm/dyn pF, independent of ϕ and T within experimental uncertainty. Our study focused on relatively low densities of the incommensurate solid phase in order to minimize second-layer occupation and desorption. In our range $0.0847\ \text{Å}^{-2}\leqslant n\leqslant0.0968\ \text{Å}^{-2}$ and $T\lesssim4$ K, second-layer densities are $<10^{-5}n$, and vapor pressures $P\lesssim10^{-6}$ Torr.[13] The gauge stability and sensitivity were adequate to detect relative fractional changes $\delta\phi/\phi\sim7\times10^{-5}$ along a single melting transition.

We measured five film isosteres over intervals of T extending well beyond the melting region. Each sample was prepared by adsorption at relatively high T to assure gas equilibrium throughout the cell, followed by slow cooling to low T. Data were usually taken at successively lower T's, with occasional cycles to higher T to check reproducibility. The capacitance responded to each change of T by approximately exponential relaxation, with characteristic times τ of several minutes. We observed the relaxation for at least 10τ before each measurement. The data are shown in Fig. 2.

At $T\lesssim0.8T_m$ the 2D pressures varies as T^3, in accord with the behavior of 2D elastic solids,[9] and the Debye temperatures agree closely with calorimetric values.[7,8] On the approach to melting the slopes increase smoothly, remain nearly constant over ~0.1 K, and then gradually decrease. The temperatures at the midpoints of the high-slope region agree with the melting boundary $T_m(n)$.[8] The linearity of the central region suggests a first-order process, but there are no discontinuities of slope as in Fig. 1. Also, the maximum slope is much smaller than that of the phase boundary. These latter features might be due to continuous melting or to heterogeneity-broadened abrupt transitions. Therefore, further analysis is required, with detailed attention to quantitative effects of heterogeneity.

The heterogeneity of the strain-gauge substrate was estimated from comparisons of Kr vapor-pressure isotherms of a sample of MAT with other exfoliated graphite materials,[14] which showed the uniformity of MAT to be comparable with the foam used in the calorimetric study.[8] We therefore assumed a heterogeneity distribution similar in form, namely a sum of a broad and a narow Gaussian, but we initially allowed the Gaussian widths and fractions to be free parameters.

Computer fits to the strain-gauge isosteres were calculated by convoluting ideal transition shapes with the heterogeneity distribution. The ideal

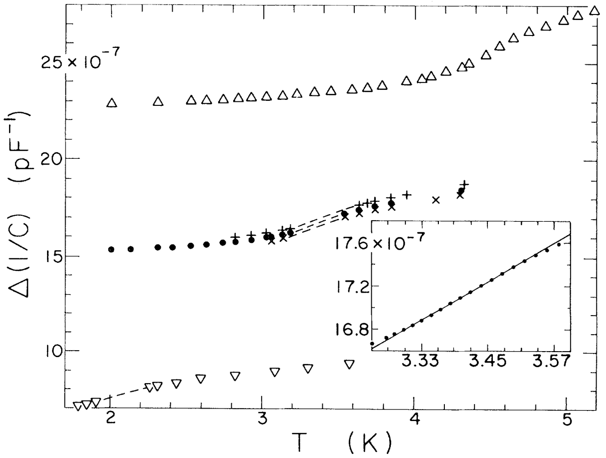

FIG. 2. Capacitance changes of the two-dimensional pressure gauge for five films in the regions of their melting transitions. Film densities in Å^{-2}: triangles, 0.0968; pluses, 0.0924; circles, 0.0922; crosses, 0.0920; inverted triangles, 0.0847. Inset shows enlargement of central portion of 0.0924 Å^{-2} film.

first-order shape was constructed by extrapolating the trends of the single-phase regions well outside of the transition, and fixing the slope in the two-phase regime to that of the extended range of the phase boundary. Thus, except for some latitude in the extrapolation of the single-phase regions, the ideal isostere is completely determined. Moreover, though the widths and relative magnitudes of the heterogeneity-distribution Gaussians had been free parameters, the values that gave the best fit to the data were in agreement with those used in the calorimetric study. Thus, all of the parameters in the final convolution were consistent with the substrate characterization. Figure 3 shows that this convolution reproduces the data to within experimental uncertainty, establishing consistency with heterogeneous first-order melting.

We also compared the results with the theory of dislocation-mediated melting,[1] via the similarity between the heat capacity and $(\partial\phi/\partial T)_n$. The theory predicts a broad specific-heat peak at a temperature above the theoretical transition T_0, due to the progressive creation and unbinding of dislocation pairs. The shape of the peak is nonuniversal, its width and height being dependent on the dislocation core energy; hence we modeled the theoretical specific heat by a Gaussian of adjustable width.

This ideal continuous melting curve was convoluted with various heterogeneity distributions in an attempt to fit the data. The best fits, however, required a peak with full width at half maximum (FWHM) $\Delta T/T_{\mathrm{peak}}$ considerably narrower than a theoretical estimate for dislocation-mediated melting. Saito[15] calculated the melting heat capacity of a dislocation vector model, for two values of core energy E_c : $E_c/kT_0 = 3.3$, 2.3. For the larger value Saito found continuous melting, with FWHM $\Delta T/T_{\mathrm{peak}} = 0.2$, Our measurements require an ideal width less than 0.2 of Saito's value. Indeed, even apart from our heterogeneity convolution, the FWHM of the entire heterogeneity-broadened experimental transition is less than one-half of Saito's width. While the theoretical width can be narrowed somewhat by reducing the core energy, the reduction is constrained by Saito's finding of a first-order transition at $E_c/kT_0 = 2.3$. Moreover, Saito's core energies are well below the experimental activation energies of excitations presumed to be dislocation pairs: $7 < E_c/kT_m < 10$.[8] The observed melting is therefore inconsistent with dislocation-mediated melting as calculated by Saito. Presently there are no calculations other than Saito's.

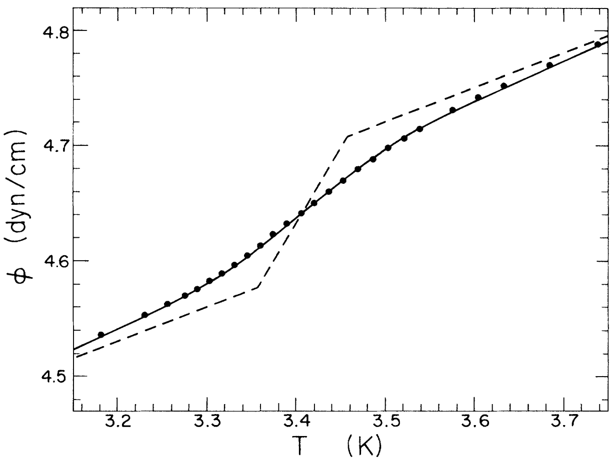

FIG. 3. Comparison between ideal and heterogeneity-broadened ideal first-order melting, and experimental results. Dashed line, 2D pressure of ideal film, constructed from single-phase behavior and slope of melting line; solid line, convolution of ideal curve with heterogeneity distribution; circles, data for film density 0.0924 Å^{-2}.

We therefore conclude that the melting of incommensurate solid ^{4}He monolayers is first order in the experimental range, and that the order of the transition cannot be explained, within the context of dislocation-mediated melting theory, by low dislocation-core energy. Narrowly construed, this result does not contradict the theory, since it admits that a first-order process may preempt the continuous transition. However, the absence of continuous melting in incommensurate He monolayers is particularly significant, since these films satisfy the model conditions so well. These results, together with recent work on Ar[16] and earlier work on other films,[4] shows that all known melting transitions in incommensurate films, at monolayer coverage or less, are first order. One must therefore question whether the continuous-melting theory is complete. Alternative mechanisms, such as grain-boundary melting,[17] should be given serious consideration.

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