Heat-Capacity and Sticking-Probability Measurements of ^{4}He Submonolayers Adsorbed on Evaporated Ag Films: Bose Statistics in Two Dimensions

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We have measured the heat capacity of submonolayers of ^{4}He adsorbed on Ag films between 1.7 and 3.3 K. Good fits to the results are obtained with a model of a noninteracting two-dimensional Bose gas. The sticking probability for room-temperature ^{4}He atoms on cold Ag has been measured as a function of substrate temperature and ^{4}He coverage. The sticking probability is 4% at low coverage, and abruptly drops to 1% for coverages above 0.5 monolayer.

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There has been much interest in monolayers of physisorbed noble gases as systems suitable for testing theoretical models of thermodynamics in two dimensions.[1,2] Experimental measurements of the heat capacity are important for the identification of the phases and the transitions between them. Such measurements are made difficult by the need to subtract the heat capacity of the physisorption substrate. This problem is usually solved by the use of insulating substrates with high specific surface area such as exfoliated graphite.

Measurements of the heat capacity of submonolayers of the Fermi gas ^{3}He adsorbed on graphite give a particularly simple result—the heat capacity of a two-dimensional Fermi gas.[3] The presence of a Fermi surface at finite energy suppresses the effects of the substrate.

The results of similar measurements with the Bose gas ^{4}He, by contrast, are dominated by substrate-induced effects.[3] The heat capacity of <0.4 monolayer of ^{4}He on graphite exhibits broad anomalies at temperatures below 2 K. Above 2 K, the heat capacity approaches that of an ideal two-dimensional classical gas. Above 10 K, excited states perpendicular to the surface become thermally excited. The low-coverage data have been given two different interpretations. The first is that the low-temperature deviation of the heat capacity from that of an ideal two-dimensional gas arises from second-order terms in the virial expansion of the ideal-gas law.[4] The second interpretation ignores the He-He interactions and treats the problem of a single ^{4}He atom moving within a laterally varying physisorption potential.[5] The periodic variations in the binding energy give rise to gaps in the density of states and anomalies in the heat capacity which resemble the experimental results. The data are perhaps best explained by some combination of these two models. The success of a model which ignores the He-He interactions serves to illustrate the degree to which the ^{4}He/graphite phase diagram has been influenced by the structure of the graphite surface.

The heat capacity of >0.8 monolayer of ^{4}He on graphite exhibits a rounded peak at temperatures above 2 K which arises from the melting of the incommensurable solid phase.[3,6–8] The peak is broadened by extrinsic effects. The characterization of this phase transition as an example of either Kosterlitz-Thouless melting or first-order melting is currently the subject of some controversy.

Thick multilayer films are well known to exhibit superfluidity. The absence of long-range order in two dimensions, however, may inhibit superfluidity in thin films.[9] The initial application of the Kosterlitz-Thouless theory to this problem predicted superfluidity at 1 K in 0.5 monolayer of ^{4}He.[10] In experiments which include a Mylar substrate, the first two layers of ^{4}He are laterally localized by the substrate. As a result, superfluidity is experimentally observed on Mylar at 1 K only for coverages greater than two layers.[11] The use of substrates which do not localize the first two layers would presumably allow the observation of superfluidity at lower coverages.

Metallic substrates represent an attractive alternative for studies of adsorbed layers because the nonlocal nature of the electronic wave functions provides a more uniform physisorption potential than for graphite.[1,12] The large low-temperature heat capacity of most metals, however, means that the problem of sensitivity will arise even when the ratio of surface area to volume is large. Metallic powders that satisfy this criterion have a complicated assortment of surfaces and would not yield interpretable results. Evaporated films, such as Ag, that have shown a high degree of orientation are perhaps the best candidates for such measurements. Scanning tunneling microscopy (STM) has shown that Ag films deposited on sapphire substrates at room temperature are composed of (111) crystallites of about 500 Å in lateral dimension, separated by compact boundary regions.[13]

We have constructed a novel ac microcalorimeter with sufficient sensitivity to measure the heat capacity of submonolayers of ^{4}He on metallic substrates. It can also be used for measurements of the heat capacity of adsorbates on any surface suitable for vacuum deposition. The design of the calorimeter shown in Fig. 1 is derived from that of the composite bolometer, which is the most sensitive broadband detector of far-infrared radiation.[14] It is composed of a single-crystal Ge:Ga thermometer, NiCr heater films, and 25-μm Cu wires, all of which are attached with conductive epoxy to the back of a sapphire substrate. The calorimeters are mounted on the end of a liquid-^{4}He-cooled cold finger in a conventional UHV system and can be operated from 1.7 to 4 K. Openings through radiation shields at 90 K can be temporarily aligned to allow deposition of a clean Ag surface or to allow dosing of the calorimeter with a beam of ^{4}He atoms from an effusion cell. Because the sticking coefficient of room-temperature ^{4}He atoms on Ag at low temperatures is not known, the final coverages are not known, except when they can be determined from the heat-capacity measurements. Measurements of the heat capacity of ^{4}He on the bare sapphire that surrounds the Ag film have been carried out.[15] These measurements indicate that either the helium is not bound to the sapphire at these temperatures so that there will be a potential barrier to migration, or it does not occupy states with lateral mobility. In either case, the sapphire constrains the ^{4}He atoms to the Ag film. The effects of migration were observed in calorimeters with a continuous metallic path from the Ag film to the heat sink.

The very short internal time constants of this calorimeter allow us to make ac heat-capacity measurements[16] at 500 Hz. An oscillation in the temperature of the calorimeter with an amplitude of ~ 1 mK is produced by the application of an ac bias to one of the heaters. This oscillation in temperature is detected as an oscillation in the voltage across the dc-biased resistance thermometer. The heat capacity is then calculated from the ratio of the power oscillation to the temperature oscillation. The temperature of the calorimeter is regulated by application of a correction voltage to the second heater. The heat capacity of the calorimeter is measured before and after the ^{4}He dose at a series of temperatures between 1.7 and 4 K. The heat capacity of the calorimeter varies from less than 3×10^{-8} to more than 3×10^{-7} J/K. Subtraction of the data for the bare calorimeter from the data for the dosed calorimeter yields the heat capacity of the adsorbed layer. Through careful control of drifts in the measured voltages, the heat capacity of less than 0.01 monolayer of an adsorbate in the gas phase can be detected. A complete description of this apparatus and the measurement technique is presented elsewhere.[15]

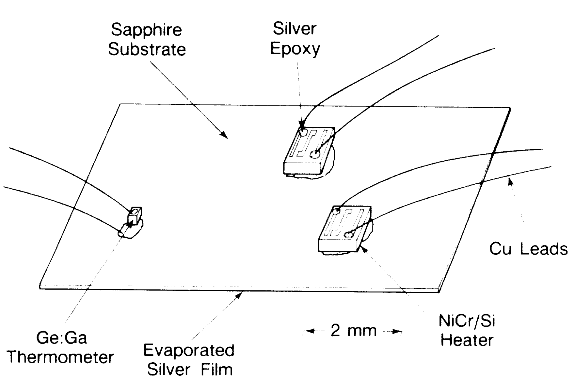

FIG. 1. Schematic drawing of the calorimeter used in these studies. Ag films are deposited *in situ* on the front of the sapphire.

The measured heat capacity for several coverages of ^{4}He adsorbed on Ag is shown in Fig. 2 as a function of temperature between 1.7 and 3.3 K. At the lowest coverages investigated, the heat capacity is independent of the temperature. As the coverage is increased, the heat capacity is seen to increase with increasing temperature and then approaches a constant value. The sensitivity of the measurement degrades with increasing temperature due to an increase in the heat capacity of the substrate and to a reduction in the sensitivity of the thermometer. More accurate measurements at the higher temperatures have been made by increasing the amplitude of the temperature oscillation. These measurements show that the heat capacity is independent of temperature between 2.3 and 3.3 K for the five lowest coverages shown. Above 3.3 K, desorption of the ^{4}He occurs.

There are a number of striking differences between these data and those for similar coverages of ^{4}He on graphite substrates. The absence of Schottky-type anomalies is taken as evidence that the corrugation in the binding energy to the Ag substrate is weaker than for insulating substrates, as expected. There is no evidence of the increase in heat capacity with decreasing temperatures predicted from the virial expansion of the adsorbate-adsorbate interaction,[4] or from a melting transition from the hexagonal incommensurable phase that is expected at low temperatures.[17]

The adsorbate-adsorbate interaction is reduced by the electrons in the metal.[18] Procedures for estimating this effect are in the literature.[19,20] At the average separations typical of the highest coverages investigated here, however, these corrections are estimated to reduce the adsorbate-adsorbate interactions by less than 5%.

Theoretical descriptions of thermodynamics in two di-

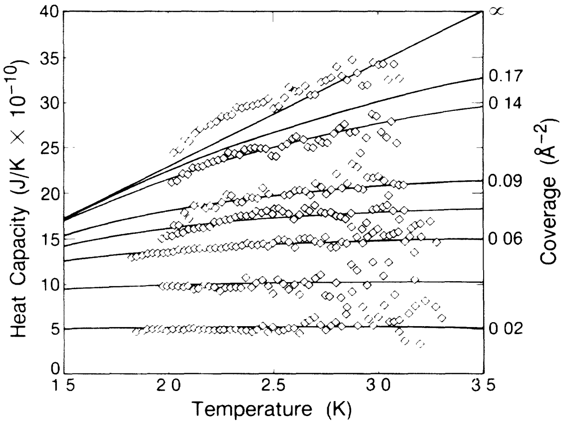

FIG. 2. Measurements of the temperature dependence of the heat capacity for a series of coverages of ^{4}He on Ag films. The solid lines correspond to the calculated heat capacity of a two-dimensional noninteracting Bose gas.

mensions which address the normal component of the adsorbate-substrate interaction include the excited states in addition to the ground state.[5] For ^{4}He on graphite, the excited states are expected[5] to lead to an increase in heat capacity with increasing temperatures above 10 K. The first excited state for ^{4}He on Ag is calculated[21] to be 1.9 meV above the ground state, compared with 5.7 meV for graphite,[22] so this contribution should appear at temperatures above 4 K. We see no evidence of this contribution to the heat capacity, up to the desorption temperature of 3.3 K.

In the presence of lateral fields, which can arise due to defects on the surface, the two-dimensional ^{4}He gas is susceptible to Bose condensation.[1,23] This effect would give rise to a linear temperature dependence at low temperatures, followed by a peak at the Bose condensation temperature. The lowest-coverage data in this experiment may be compared directly with a calculation[23] of the temperature dependence of the heat capacity for various values of the lateral field, showing that the lateral field in this experiment is 0.1 K or smaller. For all the coverages investigated, such a lateral field would be expected to induce Bose condensation at temperatures well below 1.8 K, giving rise to very small peaks in the heat capacity and only very slight perturbation from the ordinary Bose gas at the temperatures of these measurements. There is no direct evidence for a surface-induced Bose condensation from this experiment.

Since the signatures of adsorbate-adsorbate or adsorbate-substrate interactions do not appear in the data, we compare the results with the heat capacity of a two-dimensional noninteracting Bose gas.[24] The energy of the system can be written as

$$U(T)=\int_{-\infty}^{\infty}\frac{ED(E)dE}{e^{\beta(E-\mu)}-1}, \qquad (1)$$

where $D(E)$ is the density of states, μ is the chemical potential, and $\beta=(k_BT)^{-1}$. For noninteracting particles confined to a surface of area A by a potential with bound states E_i normal to the surface, $D(E)$ is given by

$$D(E)=\sum_{i}^{\text{all bound states}}\frac{2\pi mA}{h^2}\Theta(E-E_i), \qquad (2)$$

where $\Theta(E-E_i)$ is zero for $E<E_i$, and 1 for $E\geq E_i$. Since the excited states are not populated at the temperatures of interest, we consider only the ground state, for which $D(E)=(2\pi mA/h^2)\Theta(E)$. Requiring the number of bosons in the system N to be constant yields an expression for the chemical potential,

$$\mu=k_BT\ln(1-e^{-Nh^2/2\pi mAk_BT}). \qquad (3)$$

The chemical potential approaches zero at low temperatures. In this limit, the expression (1) for the energy can be evaluated exactly, and then differentiated to give $C(T)=(\pi^3k_BmA/3h^2)T$, which is independent of the number of bosons in the system. At such low temperatures, nearly all of the bosons are in the ground state of the two-dimensional system, where they do not contribute to the heat capacity. At higher temperatures, the constraint on the number of bosons in excited states due to the restriction on N becomes important, and the chemical potential takes on a finite value. As the temperature is increased, the heat capacity eventually approaches the limit $C(T)=Nk_B$ which is given by classical equipartition. This behavior is not to be confused with that of a Bose condensation, in which the fraction of bosons in the ground state suddenly becomes appreciable as the temperature is reduced to below a critical temperature. It is interesting to note that, although the physics is very different, the heat capacity of the two-dimensional Bose gas has the same form as that calculated for the two-dimensional Fermi gas.[25]

The expression (1) for the energy of the two-dimensional Bose gas has been numerically integrated, and then differentiated to give the heat capacity as a function of temperature and coverage. The coverage is adjusted to fit each data set at the highest temperatures measured. There are no other adjustable parameters, so the downward deviations at the lowest temperatures are determined by Bose statistics. These calculations are shown as smooth curves in Fig. 2. The measured deviations from the equipartition limit which occur at lower temperatures are in excellent agreement with the predictions of this model even at coverages in excess of 0.5 monolayer, as defined in terms of the monolayer coverage on graphite. At higher coverages the measured heat capacity is larger than the theoretical prediction, but the effects of adsorbate-adsorbate interactions, which are ignored in this model, may be important.

In order to obtain a measurement of the sticking coefficient, the change in heat capacity is monitored while the sample is dosed at a constant temperature. A plot of these data as a function of the exposure is shown for three substrate temperatures in Fig. 3. At temperatures above 2.5 K and heat capacities below 20×10^{-10} J/K, the heat capacity is independent of temperature and assumed to be a measure of the number of adsorbed atoms. The coverages estimated in this manner are shown on the right-hand side of Fig. 3. The derivative of the coverage with respect to the exposure is defined as the sticking probability. At the lowest coverages, the sticking probability is 4%, independent of coverage or substrate temperature. At coverages greater than 0.5 monolayer, the sticking probability abruptly decreases to about 1%. The coverage at which the sticking probability changes decreases with increasing substrate temperatures.

During sticking, the kinetic energy of the incident atom is dissipated through the creation of a small number of excitations in the substrate. Since the kinetic energy of the incident atom is much larger than k_BT of the substrate, only spontaneous emission of excitations occurs. This process should be independent of substrate temperature, as is observed at low coverage. Defects or

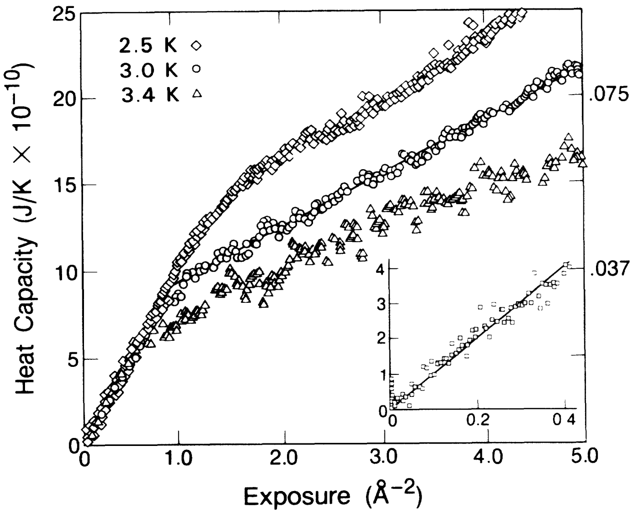

FIG. 3. Measurements of the number of adsorbed atoms as a function of the number of incident atoms for ^{4}He on Ag at various substrate temperatures. The slope of the curves shown here is the sticking probability. Inset: Data for the lowest coverages expanded. For this figure, coverages are obtained through the relation $N = C/k_B$.

impurities on the Ag surface with greater binding energy than the rest of the surface would be expected to freeze out the first adsorbed atoms. In this measurement of the sticking coefficient, such effects would appear as a nonzero x intercept corresponding to the adsorption of the first atoms in states with low heat capacity. The measured x intercept is indistinguishable from zero for coverages of less than 1% of a monolayer. The occurrence of the ideal-gas phase at such low coverages is strong evidence that the physisorption potential of the Ag film is extremely uniform.

The appearance of abrupt changes in the measured sticking probability as a function of coverage usually implies either solidification in the adsorbed layer, or layer completion and promotion into the second layer. Near such structural changes, there are corresponding changes in the entropy of the adsorbate, which should appear as large anomalies in the temperature dependence of the heat capacity. The absence of such features in the measured heat capacity weakens these explanations for the changes in the sticking probability. Any explanations that would depend on inhomogeneities in the binding energy would also give rise to a finite x intercept in the data of Fig. 3. We have no simple model for this complicated behavior in the sticking coefficient. Exotic explanations are possible but are not well constrained by the data.

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