Atomically Thin Superfluid Helium Films on Solid Hydrogen

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We have measured both adsorption isotherms and third-sound resonance of atomically thin ^{4}He films on solid hydrogen. We find helium more weakly bound to a hydrogen surface than to other rare-gas surfaces, with a van der Waals coefficient of 4.6 ± 0.4 K (layers)^3. We have also measured third sound, at 0.18 K, down to a total helium coverage of 0.45 ± 0.01 atomic layer, indicating an inert coverage at $T=0$ K of 0.29 atomic layer or less. In common with other weak-binding substrates we also see depressions in third-sound velocity near half-layer intervals.

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What happens at the boundary between a liquid and a solid or, more simply, between a superfluid and a solid? It has recently proven fruitful both experimentally [1] and theoretically [2] to ask this question in the limit of weak binding of helium on surfaces. This approach is to be contrasted with a large body of work on strong-binding substrates such as graphite [3] where phases with atomic localization and layer solidification dominate. In the weak-binding limit, zero-point motion becomes a major consideration and surface solidification in the limit of low temperature cannot be assumed even for the first layer of helium atoms. Recent calculations of Cheng, Cole, and Shaw [4] have shown that the thermodynamic state of a monolayer coverage or less of helium atoms on a sufficiently weak-binding surface can be either a gas or a liquid and is sensitive to both the long- and short-range parts of the surface potential.

In this paper we describe measurements on solid hydrogen which have clearly shown, for the first time, surface superfluidity for submonolayer coverages of helium. Measurements of adsorption isotherms [5] and third-sound resonance [1] for atomically thin films of ^{4}He on other weak- (and not so weak) binding substrates of Ar, Ne, CO_2, and Cu have shown an inert helium layer coverage of precisely 1 layer.

Measurements of both pressure and third sound at constant temperature as a function of coverage allow us to measure both the long- and short-range parts of the surface attraction, to establish the coverage and density of the inert (nonsuperfluid) layer of helium, and to accurately measure apparent structure in the helium film. The apparatus and techniques of analysis are fully described in Refs. [1], [5], and [6]. A sintered-copper film reservoir with a surface area of 4 m^2 is connected by a small capillary to a third-sound resonator. The reservoir stabilizes helium coverages during third-sound measurements. As described in Ref. [7], isotherm measurements were made in this reservoir and, for hydrogen, in a second similar reservoir. The analysis of the isotherm data [5] uses a modified Brunauer-Emmett-Teller (BET) model [7,8] for low coverage (less than 2 layers of helium) where an enhancement in density can be taken into account for the first layer. At large helium coverages (greater than 3 layers) we can accurately model the adsorption measurements using the Frenkel-Halsey-Hill (FHH) model [9] which uses the first term of a surface potential relative to the bulk chemical potential of

$$V(d) = -\Gamma/d^3 + B/d^{\varepsilon}, \quad (1)$$

where Γ is the coefficient of the van der Waals potential and d is the film thickness in units of layers, where 1 layer is 12.95 μmol/m^2. Further analysis in the transition region between low and high coverages reveals a modification of the van der Waals attraction described by a term of the opposite sign (repulsive), and $B=4.5$ K (layer)$^{\varepsilon}$, which varies as the distance from the substrate with the power $\varepsilon = 5.4 \pm 5$.

The results of this analysis are shown in Table I. The van der Waals coefficients Γ are consistent with the early phonon experiments of Sabisky and Anderson [10]. They found Γ to be 14.5 K for helium on solid argon and 6.8 K for helium on solid neon. Our results compare even more closely with the independent calculations of Cheng and Cole [11] where they obtain 27 K for helium on CO_2, 17.8 K on argon, 10.6 K on neon, and 7.7 K on hydrogen. We emphasize these results because any error in our measurements of helium coverage is raised to the third power, changing the van der Waals coefficient we calculate accordingly.

In Fig. 1 we compare the adsorption isotherms of helium on solid hydrogen to that of helium on neon to emphasize how weakly bound helium is on hydrogen. In the low-coverage limit, we found for the hydrogen substrate the poorest fit between the BET model and our data. This is reflected in the large error bars for the resultant van der Waals coefficient in Table I. On other substrates such as neon and argon the first layer of helium atoms is well characterized by a distinct binding energy. It is possible that a large zero-point motion of helium atoms, on hydrogen, in the vertical direction could render the submonolayer of helium a gas and produce a large change in the binding energy with coverage while forming the first layer. This possibility has been considered by Cheng, Cole, and Shaw [4] for helium on weak-binding substrates such as alkali-metal surfaces. This is even more likely considering that our measured van der Waals force

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TABLE I. Adsorption of helium on sintered copper and on 8–10 layers of solid gases plated on sintered copper. The analysis combines a modified BET model for low coverage and an FHH model for high coverage. Adsorption on hydrogen was measured in two different sintered-copper reservoirs. σ_1/σ_B is density, relative to bulk liquid, for the first adsorbed layer of helium; Γ is the van der Waals coefficient. Errors are determined by the F test with a 90%-confidence interval.

Substrate	Temperature (K)	Surface area (m^2)	σ_1/σ_B	Γ [K (layers)^3]
		Reservoir 1		
Cu	1.726	3.97 ± 0.21	1.36 ± 0.11	30.9 ± 4.4
CO_2	1.726	3.94 ± 0.07	1.45 ± 0.04	26.5 ± 1.5
Ar	1.726	4.23 ± 0.08	1.29 ± 0.05	17.6 ± 1.6
Ne	1.720	4.18 ± 0.16	1.10 ± 0.06	9.1 ± 1.3
H_2		4.24 ± 0.14 [a]		
		Reservoir 2		
Cu	1.688	2.83 ± 0.06	1.45 ± 0.05	29.0 ± 1.2
H_2	1.690	3.02 ± 0.1	1.00 ± 0.10	4.6 ± 0.4

[a]Found by slope of Kosterlitz-Thouless transition versus coverage.

is less than that used in their calculations, as mentioned above. From Fig. 1, it is evident for the highest-temperature adsorption isotherm for hydrogen that there is only $\frac{1}{4}$ of a layer of helium (or 0.3 $Å^2$/atom) that seems bound to the hydrogen surface, in contrast to neon.

The results for the velocity of third-sound versus helium coverage were unusual, and measurements were carried out in two different resonators using the helium film reservoir in different ways. Measurements were first taken using the well-characterized copper surface, from earlier third-sound and adsorption measurements, of the helium film reservoir. This reservoir, connected to the third-sound resonator with a long 3-μm-i.d. quartz capillary, allowed us to form a 10-atomic-layer substrate within the third-sound resonator with hydrogen gas without contaminating the copper surfaces of the reservoir. In the superfluid state, using chemical-potential equilibrium between coverages in the reservoir and the resonator and independent measurements of chemical potential from adsorption, we related coverage in the resonator to the measured coverage in the reservoir. The third-sound velocity data using this coverage scale are shown as the solid line in Fig. 2. A new resonator was installed and connected to the helium film reservoir by a short stainless-steel tube with a 125 μm i.d. In this case, with pressure equilibrium, both the reservoir and the resonator surfaces were covered with 10 layers of hydrogen. The reservoir then directly indicated coverage in the third-sound resonator. The data from these measurements are shown as the crosses in Fig. 2. There are no significant differences between the two sets of data.

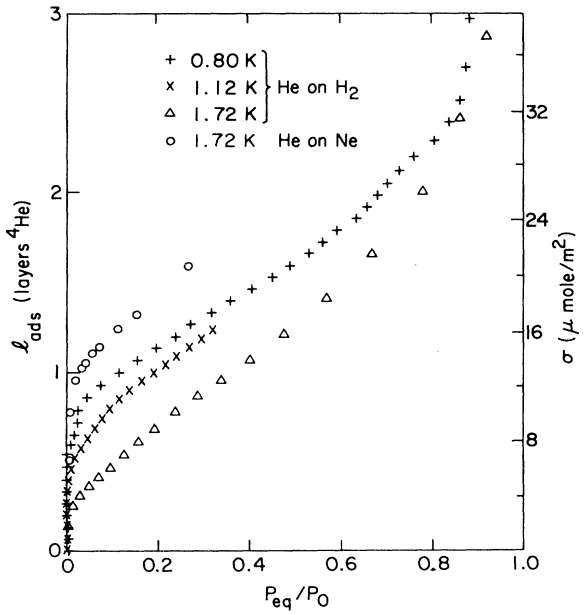

FIG. 1. Comparison of adsorption isotherms for helium on hydrogen and helium on neon. At 1.72 K, the coverage for helium on hydrogen is half that for helium on neon at $P_{eq}/P_0 = 0.2$ indicating much weaker binding on hydrogen. Note the sharp rise for the 1.72-K measurement of helium on hydrogen, near $P_{eq}/P_0 = 0$, to 0.25 layer. Adsorption of helium on hydrogen at 0.8 K, with pressures measured *in situ*, indicates an approach to layer completion near zero relative pressure—yet more than one-half of that layer displays superflow.

There are two qualitative features seen from the measurements of the third-sound velocity of helium on solid hydrogen. First, third sound is seen down to a total helium coverage of 0.45 layer, at 0.18 K, near its Kosterlitz-Thouless (KT) transition [12]. Measurements of the KT transition temperature for a range of total submonolayer coverages were extrapolated to zero temperature, as shown in Fig. 2. We find, at $T = 0$, superflow would first be seen at a total helium coverage of 0.29 layer or less on solid hydrogen. We measured the KT transition temperature of helium on hydrogen as a function of total coverage, taking measurements at coverages corresponding to

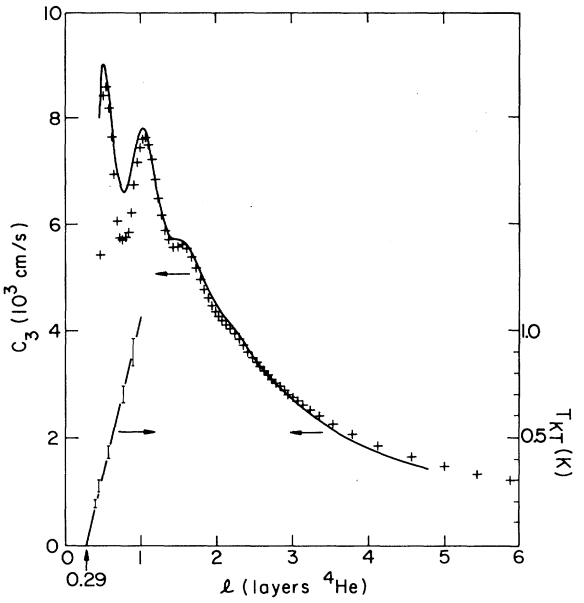

FIG. 2. Third-sound velocity vs coverage of ^{4}He on a hydrogen substrate at 0.18 K. The solid curve represents measurements taken with a coverage scale determined by helium on sintered copper using chemical-potential equilibrium. The crosses are measurements with a coverage scale determined directly by helium on solid hydrogen. The two experiments give essentially the same results. Superflow is seen down to a total helium coverage of 0.45 layer. The right-hand scale displays the measured Kosterlitz-Thouless transition temperatures for the indicated coverages.

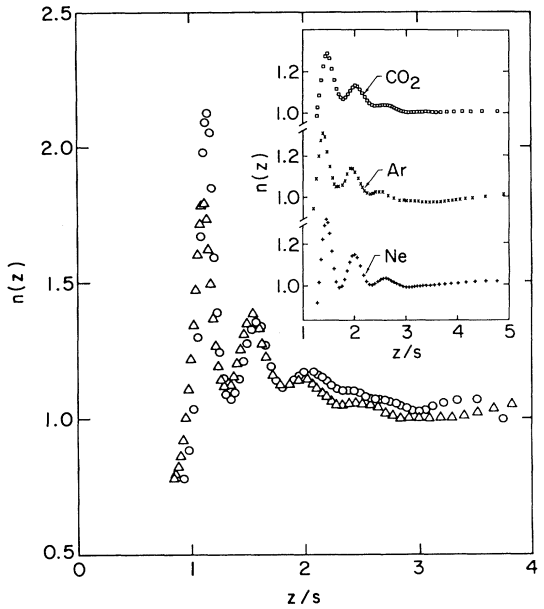

FIG. 3. Surface density vs thickness of a helium film on hydrogen, assuming that this can explain third-sound variations with coverage. $n(z)$ is normalized to bulk liquid density. The triangles are from the data indicated by the solid line in Fig. 2 and the circles are from the crosses in Fig. 2. Note the peaks in the surface density at half-layer intervals. The first large peak indicates the completion of the first layer of helium while in the superfluid phase. As shown by the inset, from Ref. 1, this half-layer phenomenon is seen on other weak-binding substrates and accurately superimposes on the results of helium on hydrogen.

the local minima and maxima of the third-sound velocity. We find that these minima and maxima do not affect the KT transition temperature, and that all of these measurements fall on a straight line (as seen in Fig. 2), as expected by the KT model. We can use a factor of 0.82, obtained from the work of Agnolet, McQueeney, and Reppy [13], for the ratio of the superfluid coverage at the KT transition to the total helium coverage that can be considered superfluid well below the KT transition temperature. With this correction the slope of the measured KT transition temperature versus coverage independently gives a reservoir area of 4.24 m^2, within 6% of the values obtained by adsorption analysis for other substrates in this reservoir as shown in Table I.

The second feature, seen in Fig. 2, is the periodic depression of third-sound velocity as a function of coverage. Surprisingly, the depressions fall at approximately half-layer intervals. The KT analysis discussed above shows that these depressions are not due to changes in the areal superfluid fraction. When third sound is measured on stronger-binding substrates such as CO_2 the relative size of these depressions becomes smaller. On graphite surfaces, strong signatures are seen only at helium layer completion in the third- and fourth-sound velocities [14] with no effects seen at half-layer coverage. The calculations of helium layering by Mikheev and Chernov [15] and by Krotschek [16] show smectic density waves within a helium film, but only with a periodicity of 1 layer. We can analyze the data with a general expression for third-sound velocity from Goodstein [17], which only assumes a helium film with vertical equilibrium:

$$C_3^2 = \frac{\sigma_s}{m}\frac{\partial \mu}{\partial z} \Big/ \frac{\partial \sigma}{\partial z}, \tag{2}$$

where σ and σ_s are the areal mass density and superfluid mass density, respectively, m is the atomic mass of helium, μ is the chemical potential per atom, and z is the film thickness. We have expanded this expression to bring out the relation between film coverage and thickness. If the film undergoes periodic compression as the coverage is increased then it is this last differential that will modify the third sound, which we call $n(z)$. Since we find these features to be independent of a wide range of substrates, it is reasonable to assume that they are not due to variations in the chemical potential with film thickness. Figure 3, using $n(z)$, provides a comparison with other measurements in Ref. [1] on neon, argon, and carbon dioxide substrates. After the first peak, which can only be seen on the hydrogen substrate, the data from the other sub-

strates, shown in the inset, accurately superimpose.

There are two other experiments with thin helium films that can be interpreted to show half-layer phenomena. McQueeney *et al.* [18] report the sharpest superfluid transitions at film thicknesses of 1.7, 2.2, 2.65, and 3.2 atomic layers, essentially at half-layer intervals. In the experiments of Paalanen and Iye [19] and of Cieslikowski, Dahm, and Leiderer [20], measurements of electron mobility above helium films absorbed on hydrogen have shown peaks which, when interpreted as half layers (reducing calculated energies by $\frac{1}{8}$), give a reasonable van der Waals coefficient, less than that of neon, as must be the case from Fig. 1.

Considering that no calculation, as yet, has given any indication of half-layer density waves, it is worthwhile to look for another explanation than that illustrated in Fig. 3. Since the half-layer effect is general for several weak-binding substrates, we cannot use an explanation peculiar to the hydrogen substrate. Equation (2) was found assuming that the helium film formed a single dynamical system. We speculate that in the weak-binding limit layering must be considered in the equations of motion, as in the case of ^{3}He on top of ^{4}He [21]. For layers of ^{4}He on ^{4}He there would be no damping and a more complex dependence of the third-sound mode with coverage would result. At half coverage there would be a maximum in compressibility of that layer; at full coverage there would be layer promotion and a new mode appearing.

To summarize, we have found helium on a solid hydrogen substrate, with a measured van der Waals coefficient of 4.6 ± 0.4 K, to undergo superflow down to coverages of 0.45 layer, indicating a zero-temperature inert coverage of less than 0.3 layer. Thus, an inert layer of helium is not a necessary boundary condition for a superfluid-solid interface. We have also found half-layer depressions in the third-sound velocity for low coverages consistent with the results on other weak-binding substrates.

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