Tuning the Wetting Transition: Prewetting and Superfluidity of ^{4}He on Thin Cesium Substrates

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We have deposited cesium with monolayer thickness resolution on to the surfaces of a low-temperature quartz microbalance. By controlling the cesium thickness from 1 to 25 monolayers, we have been able to continuously tune the substrate adsorption potential and observe its effect on the ^{4}He prewetting phase diagram. The wetting temperature can be conveniently adjusted between 1 and 2 K. Features in both the frequency shift and the dissipation of the microbalance were used to map out the superfluid-normal boundary in the prewetting phase diagram. The transition from thin normal to thick superfluid occurs without the dissipation peak characteristic of a Kosterlitz-Thouless transition.

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It has been known for over 15 years that the alkali metals, and particularly cesium, have very weak adsorption potentials [1]. Only recently, however, it has become clear [2-4] that the phases and phase transitions of adsorbates on these weak binding substrates can be qualitatively different from those observed on conventional strong binding substrates, and several recent experiments [5-8] have confirmed novel behavior in alkali metal adsorption systems. These results have been especially provocative in the case of ^{4}He adsorption because alkali metals are the only known substrates which are not completely wet by superfluid helium, and also because this system is a particularly clear example of a more general type of surface phase transition known as prewetting [9,10]. Prewetting is a first order phase transition between thick and thin states of the unsaturated film [11,12]. It is characterized thermodynamically by nonmonotonic behavior of $\mu(d)$, the film chemical potential as a function of the film thickness. In the case of ^{4}He on cesium, this nonmonotonic behavior can be traced to the fact that at short distances, the He-Cs potential is weaker than the He-He potential, while at larger distances, the reverse is true. In previous work [10], we have used adsorption isotherms measured using a quartz microbalance to map out the phase diagram of ^{4}He/Cs. The main features of the phase diagram are a wetting transition at liquid vapor coexistence at approximately 2 K, with the prewetting line emanating from it and terminating in a prewetting critical point. These experiments were performed on cesium film substrates which were so thick (approximately 300 Å) that the adsorption potential is expected to be indistinguishable from bulk cesium.

In the experiments reported here, we have studied ^{4}He adsorption on cesium substrates (deposited on gold electrodes) which are only a few monolayers thick. By varying the cesium substrate thickness from 1 to 25 monolayers, we can tune the adsorption potential from essentially goldlike to bulk cesiumlike. These variations in the adsorption potential generate corresponding changes to $\mu(d)$ and the phase diagram. In particular, the wetting temperature at liquid-vapor coexistence is sensitively dependent on the substrate potential; by sequentially adding layers of cesium, we have systematically altered the wetting properties of the substrate from $T_w=0$ (no wetting transition) to $T_w>2$ K.

Although wetting and prewetting transitions are expected to occur in a wide variety of classical systems ranging from binary liquid mixtures to magnets, the adsorbed phases of quantum fluids such as ^{4}He are particularly interesting because of the possibility of superfluidity. In our previous investigations, the wetting temperature was so close to $T_\lambda=2.17$ K that it was experimentally difficult to detect superfluid onset. The ability to prepare surfaces with wetting temperatures substantially lower than T_λ allows us to map out the superfluid-normal boundary in the thick phase, and to examine the intersection of this line with the prewetting line. We find that the transition from thick normal to thick superfluid is accompanied by the conventional experimental signatures of mass decoupling and enhanced dissipation [12-14], while the transition from thin normal to thick superfluid across the prewetting line does not have these signatures.

The cesium substrates used in this experiment were formed by evaporating elemental metal onto both surfaces of a quartz microbalance mounted inside a vacuum can immersed in a liquid ^{4}He bath. Details of the apparatus have been described previously [9]. When helium vapor is introduced into the vacuum can, an adsorbed helium film forms on the substrate, which slightly alters the acoustic and electrical properties of the microbalance. Shifts in the resonant frequency of the crystal can be related to the adsorbed mass, while changes in the real part of the electrical impedance are related to dissipative processes in the adsorbed film [15]. In this experiment, the microbalance is used not only to detect the state of the adsorbed helium film, but also to monitor the deposition of the cesium. After each sequence of helium isotherms, the temperature of the apparatus was raised to 4 K, and the helium was pumped out. The cesium was deposited onto the microbalance at 4 K at a rate of 0.01 layer/sec. The cesium thickness was calculated from the frequency shift, assuming the film had a bulk density of 2.0 g/cm^3,

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with 1 layer=4.8 Å. This low deposition rate is apparently crucial for forming high quality films at low temperature; depositions at rates of 1 layer/sec produced porous films with anomalously high specific area.

The primary data in these experiments consist of the frequency shift, Δf, and the electrical resistance, R, of the microbalance as a function of P/P_0, the ratio of the helium pressure in the can to the saturated vapor pressure at the ambient temperature. Typical behavior of Δf and R as a function of P for a substrate consisting of 4.2 layers of Cs on the Au electrodes for two representative temperatures (both greater than T_w) are shown in Fig. 1. Both Δf plots show a flat portion at low values of P/P_0, with a step characteristic [9–12] of the prewetting thin → thick transition and a divergence at $P/P_0=1$ corresponding to wetting at liquid-vapor coexistence. The flatness of the low pressure part of the isotherm and the steepness of the prewetting step suggest that the thin cesium substrate is at least as homogeneous as the thicker substrates previously investigated. Even for cesium coverages of 2.7 layers, there are no indications of regions of bare gold, which would produce a continuously rising background in the Δf isotherms, and features in both Δf and R at the superfluid transition on gold [9].

Figure 1(c) shows an additional downward step in Δf which is associated with superfluid onset and is due to viscous decoupling of the superfluid fraction of the film. Figure 1(d) shows that a peak in R occurs at the same pressure as the downward step in Δf. These features are the well known signature of a Kosterlitz-Thouless (KT) superfluid transition, which has been extensively studied on conventional substrates [16]. The theory [14] of the dynamic response of the vortices in 2D films quantitatively accounts for the size of the features at the transition in Figs. 1(c) and 1(d). The size of the dissipation peak predicted by the theory is indicated by the bar in Fig. 1(d). Similarly, the size of the downward step in Δf is within 10% of the predicted value. In contrast, isotherms measured at lower temperatures, such as Figs. 1(a) and 1(b), do not have these characteristic features of a KT transition.

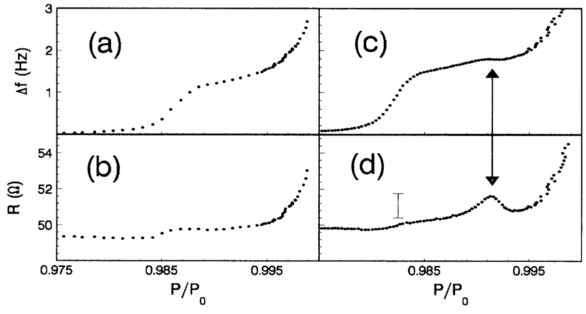

FIG. 1. Frequency shift Δf and resistance R isotherms measured at 5 MHz for a substrate composed of 4.2 layers of cesium on gold. (a),(b) $T=2.01$ K. The steep rise in Δf marks the prewetting transition. Although the thin phase is normal, and the thick phase is superfluid, there is only a small shoulder in the R isotherm. (c),(d) $T=2.08$ K. As the pressure is increased, these isotherms first cross the prewetting line and then the normal-superfluid boundary. At the prewetting transition, Δf rises abruptly, but the dissipation is hardly affected. At superfluid onset, there is a dip in Δf and a peak in R marked by the arrow. The bar shows the size of the peak in R predicted by the theory of Ref. [14].

The difference between these two types of behavior can be understood by examining the phase diagram in the P-T plane constructed from a series of isotherms in the temperature range 1.3 to 2.5 K. The features illustrated in Fig. 1 are used to locate the position of the prewetting and KT transitions, as shown in Fig. 2. The solid line marks the prewetting step [17], while the dashed line marks the KT superfluid transition; these lines are fits by functional forms based on thermodynamic descriptions [18] of these transitions, as discussed in Ref. [4]. The wetting temperature, defined by the intersection of the prewetting line with the bulk coexistence curve, is approximately $T_w=1.5$ K for this value of the cesium thickness. The KT line extends from T_λ at bulk coexistence to $T=2.05$ K where it meets the prewetting line and terminates. Isotherms taken at temperatures above this intersection, such as Figs. 1(c) and 1(d), illustrate the case in which prewetting and the KT transition are independent phase transitions of the adsorbed film.

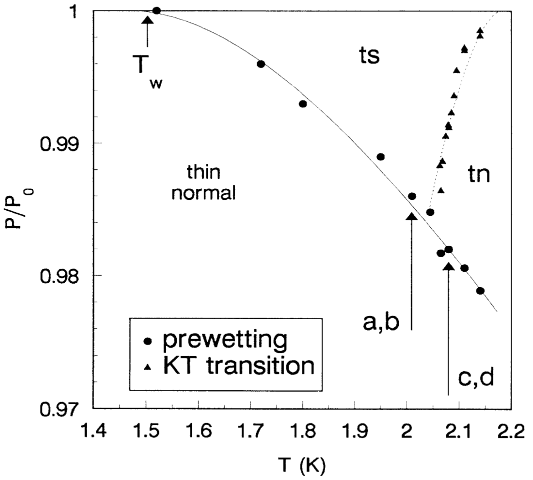

FIG. 2. P-T phase diagram for ^{4}He adsorbed on a thin cesium substrate. The circles show the position of the prewetting step for a substrate composed of 4.2 layers of cesium on gold. For this cesium thickness, $T_w=1.5$ K. The triangles show the position of the KT transition for substrates with cesium thickness ranging from 2.7 to 8 layers; the cesium thickness does not affect the position of the superfluid transition. The solid and dashed lines are fits to functional forms from Ref. [4]. ts and tn mark the thick superfluid and thick normal fluid regions. The isotherms in Fig. 1 were measured along the arrows marked a,b, and c,d.

Isotherms measured at lower temperatures, such as Figs. 1(a) and 1(b), indicate that prewetting in this regime involves a first order transition from a thin normal phase to a superfluid thick phase. The fact that the height of the prewetting step in Fig. 1(a) is smaller than in Fig. 1(c) is due to decoupling of the superfluid fraction of the film in the thick phase. In fact, the difference in heights of the steps is roughly equal to the frequency shift observed at the superfluid transition in 1(c). In Fig. 1(d) there is only a small shoulder in the dissipation corresponding to the prewetting step, since the normal fluid is essentially clamped to the substrate by viscosity. In Fig. 1(b), there is a larger step in the dissipation due to the previously observed [14] (but not fully understood) higher dissipation in the superfluid film. Dissipation peaks as illustrated in Fig. 1(d) arise when the distance between vortices (which depends on film thickness) becomes equal to the vortex diffusion length. On the prewetting line there is a discontinuity in the film thickness, and the conditions for maximum dissipation are not met.

The position of the prewetting line shown in Fig. 2 depends sensitively on the cesium film thickness. For cesium less than 1.5 layers thick, adsorption isotherms were almost indistinguishable from ones taken on bare gold, even at the lowest temperatures (1.3 K) we could reach. For a cesium thickness of 2.5 layers, the prewetting step was clearly visible, but the prewetting line could not be extrapolated to a positive wetting temperature using the expected thermodynamic formula [4]. For a cesium thickness greater than 2.5 layers, the prewetting line shifted to higher temperature, and the wetting temperature could be determined either by extrapolating the position of the prewetting step to $P/P_0=1$ or by monitoring the highest temperature at which hysteretic behavior in the film thickness could be observed along the liquid-vapor coexistence curve, as discussed in our previous work [10]. The dependence of T_w on cesium thickness is shown in Fig. 3. The results suggest that T_w becomes greater than zero at a thickness between 3 and 4 layers, rises rapidly between 4 and 8 layers, and varies much more slowly above 10 layers as it asymptotically approaches its bulk value [19]. The observed dependence of T_w on cesium thickness is similar to recent theoretical predictions [20], which are shown as the solid curve in Fig. 3.

As the cesium thickness is varied, the prewetting line changes in both position and slope, with the line becoming more parallel to the coexistence curve as the cesium thickness and the wetting temperature are reduced. In contrast, the KT transition occurs at the same value of P/P_0 (to within the experimental resolution of approximately 1 part in 10^4) for all the substrates investigated, as shown in Fig. 2. This is not surprising, since the suppression of the superfluid transition temperature in films of thickness comparable to the bulk correlation length is due to finite size effects [21,22] which should depend only weakly on the substrate potential.

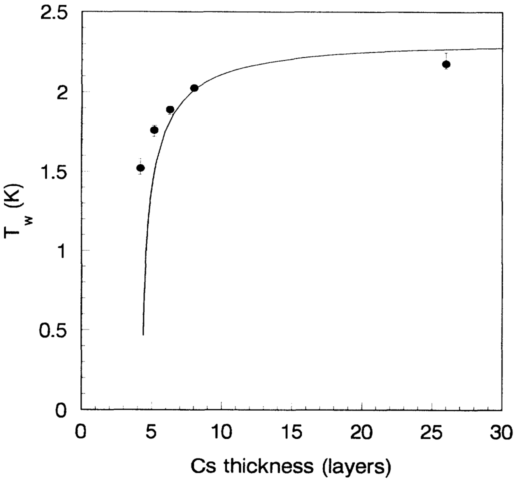

FIG. 3. T_w as a function of cesium thickness. The solid curve is the prediction of the theory in Ref. [20].

We have shown that varying the thickness of cesium on a substrate provides a convenient method of tuning the helium adsorption potential and the wetting temperature over a wide range. In contrast to more complicated chemical surface preparation techniques, the mechanism of tuning the wetting properties is simple and the interactions are well defined so that a detailed microscopic analysis is feasible. It is remarkable that cesium films can be deposited at low temperature which are only a few atomic layers thick but are nevertheless apparently quite homogeneous. The ability to depress the wetting temperature is an enabling technology for a variety of surface phase transition investigations, including the first experimental observation of the interplay between the prewetting and superfluid transitions presented here. Near T_λ, the conventional picture of a Kosterlitz-Thouless transition and finite size scaling describes our observations of the thick-normal to thick-superfluid boundary very well. At lower temperatures, the prewetting line marks an unusual first order transition from thin normal to thick superfluid which is peculiar to weak binding substrates. We anticipate that the ability to tune the substrate potential will play an important role in searches for superfluidity of adsorbed hydrogen, since a balance must be struck to achieve an adsorption potential strong enough to have liquid density but weak enough to avoid solidification.

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[1] E. Zaremba and W. Kohn, Phys. Rev. B **15**, 1769 (1977).
[2] E. Cheng, M. W. Cole, W. F. Saam, and J. Treiner, Phys. Rev. Lett. **67**, 1007 (1991).
[3] E. Cheng, M. W. Cole, W. F. Saam, and J. Treiner, Phys. Rev. B **46**, 13967 (1992).
[4] W. F. Saam, J. Treiner, E. Cheng, and M. W. Cole, J. Low Temp. Phys. **89**, 637 (1992).

[5] P. J. Nacher and J. Dupont-Roc, Phys. Rev. Lett. **67**, 2966 (1991).

[6] K. S. Ketola, S. Wang, and R. B. Hallock, Phys. Rev. Lett. **68**, 201 (1992).

[7] E. Cheng, G. Mistura, H. C. Lee, M. H. W. Chan, M. W. Cole, C. Carraro, W. F. Saam, and F. Toigo, Phys. Rev. Lett. **70**, 1854 (1993).

[8] E. Lerner, R. Morley, and O. E. Vilches, J. Low Temp. Phys. **89**, 593 (1992).

[9] P. Taborek and J. E. Rutledge, Phys. Rev. Lett. **68**, 2184 (1992).

[10] J. E. Rutledge and P. Taborek, Phys. Rev. Lett. **69**, 937 (1992).

[11] M. Schick, in *Liquids at Interfaces,* Proceedings of the Les Houches Summer School, Session XLVII, 1988, edited by J. Charvolin, J. F. Joanny, and J. Zinn-Justin (Elsevier, New York, 1991), and references therein.

[12] S. Dietrich, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. Lebowitz (Academic, London, 1988), Vol. 12, and references therein.

[13] Marvin Chester and L. C. Yang, Phys. Rev. Lett. **31**, 1377 (1973).

[14] V. Ambegaokar, B. I. Halperin, D. R. Nelson, and E. D. Siggia, Phys. Rev. B **21**, 1806 (1980).

[15] M. J. Lea, D. S. Spencer, and P. Fozooni, Phys. Rev. B **39**, 6529 (1989).

[16] D. J. Bishop and J. D. Reppy, Phys. Rev. B **22**, 5171 (1980).

[17] As discussed in Ref. [8], a step in the isotherms persists far above the prewetting critical point. We are unable to determine the critical point in these samples because of the complications of the superfluid transition and the temperature dependence of the superfluid fraction of the film.

[18] The equation of the solid line is $T\ln(P/P_0) = -1.01 \times ([\sigma_{lv}(T_w) - \sigma_{lv}(T)]/\sigma_{lv}(0))^{1.5}$, where $\sigma_{lv}(T)$ is the liquid-vapor surface tension. The equation of the dashed line is $T\ln(P/P_0) = -3.42(1 - T/T_\lambda)^{1.71}$.

[19] It is interesting to note that the wetting temperature for films thicker than 8 layers is higher than the 1.95 K that we reported previously for cesium substrates deposited at higher temperatures and higher rates. A possible explanation for this dependence of the wetting temperature on details of the substrate preparation is the variation of the wetting properties with crystallographic orientation suggested by M. W. Cole, M. R. Swift, and F. Toigo, Phys. Rev. Lett. **69**, 2682 (1992).

[20] E. Cheng, M. W. Cole, W. F. Saam, and J. Treiner, J. Low Temp. Phys. **89**, 739 (1992).

[21] F. M. Gasparini, G. Agnolet, and J. D. Reppy, Phys. Rev. B **29**, 138 (1984).

[22] Y. Y. Yu, D. Finotello, and F. M. Gasparini, Phys. Rev. B **39**, 6519 (1989).