Prewetting Phase Diagram of ^{4}He on Cesium

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We have studied the adsorption of ^{4}He on cesium in the temperature range from 1.3 to 4.1 K. The ^{4}He film undergoes a first-order phase transition known as prewetting. The prewetting line intersects the coexistence curve at the wetting temperature, $T_w = 1.95$ K, and terminates at $T_c = 2.5$ K, the prewetting critical point. There are dramatic hysteresis effects when the temperature of the system is varied at coexistence in the vicinity of T_w. This is the first experimental realization of a complete prewetting phase diagram.

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On weak binding substrates, the interaction of an adatom with the surface can become comparable to the interaction of the adatoms with each other, and subtle free energy tradeoffs have large qualitative effects on the growth [1-5] and properties [6,7] of an adsorbed film. If, for example, a coexisting liquid and vapor are placed in a container at low temperature with sufficiently weakly binding walls, the walls will typically be covered with a fluid film that is only a few monolayers thick, i.e., they will be nonwet. As the temperature is raised, the energetic cost of forming a liquid-vapor interface (the liquid-vapor surface tension) decreases, while the entropy of the film increases. Calculations [8-10] show that for many model systems the free energy of the film becomes equal to that of the bulk liquid at a characteristic temperature T_w, the wetting temperature. For $T \geq T_w$, a macroscopically thick film wets the walls at coexistence. The phase transition between nonwet and wet walls can be either continuous or first order. If the transition is first order, with a discontinuous jump in the film thickness on the coexistence curve, thermodynamics requires that a phase boundary extend smoothly into the region of unsaturated films with $\mu < \mu_{\text{coex}}$. The phase boundary which separates regions of thick and thin films is known as the prewetting line, and is expected to terminate at a prewetting critical point. Although the prewetting line is a generic feature of a first-order wetting transition and its existence was first predicted 15 years ago [11], it has not been previously observed.

Cheng, Cole, Saam, and Treiner (CCST) [1] have recently shown that the interaction of helium with substrates made of alkali metals is more than an order of magnitude weaker than with conventional substrates such as graphite. They also suggested that the phenomena of nonwetting and prewetting might be observable in these systems. Their calculations stimulated a number of experimental investigations [2-5] which have shown that adsorption on these substrates is highly anomalous. In this paper we present measurements of the complete wetting phase diagram for helium on cesium. We show that a first-order wetting transition occurs on the coexistence curve at $T_w = 1.95$ K. Isotherms above T_w show an abrupt step in the film thickness at pressures below the saturated vapor pressure characteristic of prewetting. Below T_w, there are large hysteresis effects and the film thickness of coexistence depends critically on the experimental path.

The experimental technique we have used in this study is to form a cesium substrate by evaporating elemental metal onto the surface of a quartz microbalance mounted inside a vacuum can immersed in liquid ^{4}He. When helium vapor is introduced into the vacuum can, an adsorbed helium film forms on the cesium. The mass of the adsorbed helium is monitored by observing the shifts in the resonant frequency of the crystal, which needs to be corrected for effects due to the viscosity and pressure of the gas. The mass sensitivity is approximately 5 monolayers of helium per hertz of frequency shift. We have taken particular care to avoid contamination of both the cesium and the helium since even parts per 10^6 concentrations of oxygen could alter the adsorption potential of the cesium substrate. Further details of the apparatus are described in Ref. [4].

Since our initial work reported in Ref. [4], we have compared helium adsorption isotherms on cesium films prepared at different temperatures and deposition rates. Although the isotherms are qualitatively similar, the numerical value of the frequency shift at the saturated vapor pressure is strongly dependent on the details of the evaporation procedure. We have found that cesium films evaporated onto a 4-K substrate, or onto a substrate above 150 K, yield isotherms with anomalously large frequency shifts at saturation. These films are presumably rough or porous, and behave as if the effective area of the substrate had increased by more than a factor of 5 over the geometric area. Isotherms below T_w are particularly sensitive to film quality. There, roughness apparently promotes the growth of thick films that are in fact not the equilibrium state on smoother substrates. For example, the apparent wetting behavior below 1.95 K observed by Ketola, Wang, and Hallock [3] and by us [4] in previous work is presumably due to surface imperfections in the evaporated cesium films that favor the formation of the metastable phase. The data reported here were taken on cesium films prepared at 100 K, which yielded the most vertical risers on the prewetting line, as discussed below, as well as frequency shifts at saturation above 1.95 K comparable with those on gold substrates. Capillary condensation due to surface inhomogeneity was not important in this experiment, since isotherms taken by adding gas to the system were indistinguishable from those taken by pumping gas out of the cell.

The primary data in these experiments consist of the frequency shift of the oscillator Δf as a function of P/P_0, the ratio of the helium pressure in the can P to the saturated vapor pressure at the ambient temperature P_0. Representative isotherms at three different temperatures are shown in Fig. 1. All of the isotherms show a flat portion at low values of P/P_0, corresponding to a film a monolayer or less thick [4]. The 3.35- and 2.086-K isotherms show nearly vertical rises at $P/P_0 = 1$, corresponding to a rapidly thickening film at liquid-vapor coexistence. Since the surface is wet at coexistence, these temperatures must exceed the wetting temperature T_w. Isotherms at $T > T_w$, as shown in Figs. 1(a) and 1(b), have an additional step at intermediate values of P/P_0. The location of the steps can be characterized by the reduced pressure at the inflection point of the step, $P_{\rm step}/P_0$. At high temperature [Fig. 1(a)], the step is small, rounded, and occurs far from P_0, while for temperatures close to T_w [Fig. 1(b)], the step is larger, steeper, and occurs very close to P_0. The positions of the steps measured in a series of isotherms such as those in Fig. 1 define a curve in the P-T plane, shown in Fig. 2. The portion of this curve below a prewetting critical temperature $T_w^{\rm pw}$ is a line of first-order phase transitions between thin and thick films called a prewetting line. The wetting transition temperature T_w, which is the temperature at which the prewetting line intersects the bulk liquid-vapor coexistence curve, is determined by extrapolating the values of $P_{\rm step}/P_0$ shown in Fig. 2 to the coexistence curve, represented by the horizontal line $P/P_0 = 1$. $P_{\rm step}$ and P_0 become experimentally indistinguishable at 1.95 K. This establishes the wetting temperature [12].

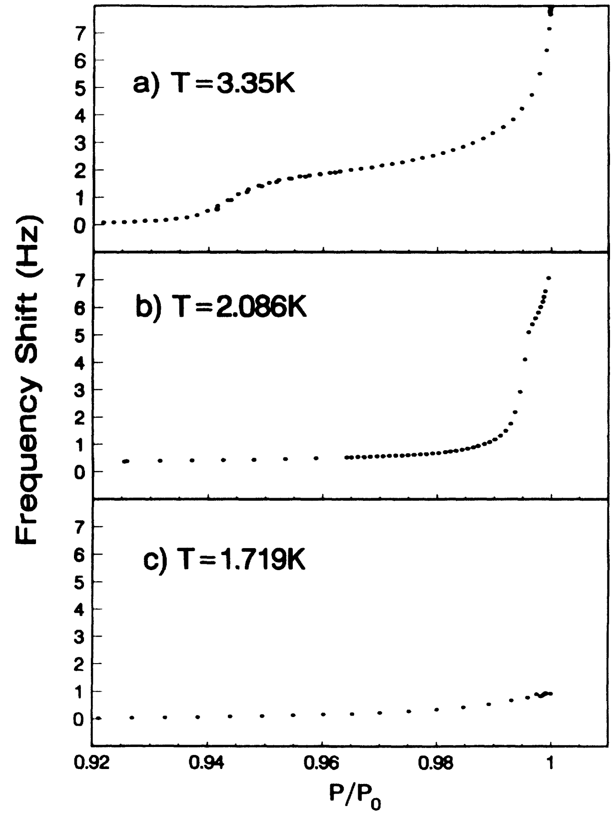

FIG. 1. Adsorption isotherms measured at 11 MHz. Film thickness in atomic layers is 5 times the frequency shift in Hz. The maximum frequency on each isotherm is $\Delta f_{\rm sat}$. Isotherm (a) is measured above $T_c^{\rm pw}$. A step in the isotherm at $P/P_0 = 0.945$ persists above $T_c^{\rm pw}$ but is not due to two-phase coexistence. Isotherm (b) is measured above T_w but below $T_c^{\rm pw}$. The maximum slope at the step at $P/P_0 = 0.995$ is over an order of magnitude steeper than the maximum slope on isotherm (a). Isotherm (c) is measured below T_w. Less than five atomic layers cover the substrate at coexistence.

A prewetting critical point at which the distinction between thin and thick phases disappears should lie on the $P_{\rm step}$ vs T curve in Fig. 2. To find the prewetting critical temperature $T_c^{\rm pw}$ the steps in the isotherms above T_w must be examined. A first-order prewetting transition on a perfectly homogeneous substrate would have a vertical rise at the step in the isotherm, corresponding to a coexistence of the thin and thick phases at constant chemical potential, or, equivalently, at constant pressure. Above $T_c^{\rm pw}$, there is no coexistence region, and the film thickens over a range of chemical potential, which results in a nonvertical (but possibly very steep) step in the isotherm. In practice, these two types of isotherms can be difficult to distinguish. To find $T_c^{\rm pw}$, which marks the high-

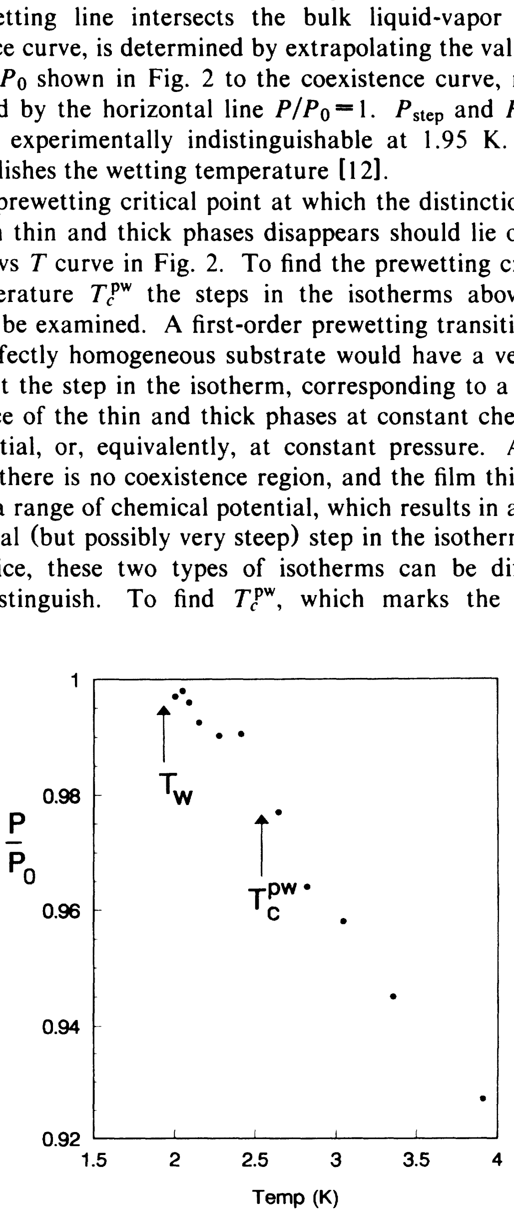

FIG. 2. $P_{\rm step}/P_0$ vs T. The intersection of this curve with the line $P_{\rm step}/P_0 = 1$ locates the wetting temperature. The critical temperature, $T_c^{\rm pw}$, determined from Fig. 3, marks the end of the two-phase thick-thin coexistence region.

temperature end of the prewetting line, we calculate $(d\mu/d\Delta f)_T$ through the step for each isotherm using the relationship $\mu = T\ln(P/P_0)$, and find the minimum value $(d\mu/d\Delta f)_{\min}$. This derivative corresponds to the inverse of the maximum slope on the steps on the isotherm. Since Δf is proportional to the adsorbed mass, $(d_\mu/d\Delta f)_{\min}$ would be identically zero in the two-phase coexistence region on an ideal substrate. Figure 3 shows $(d\mu/d\Delta f)_{\min}$ as a function of T. Below 2.5 K it has a small nearly constant value. Above this temperature the curve is much steeper and increases by an order of magnitude over the next degree. This indicates that T_c^{pw} is 2.5 ± 0.1 K. The nonzero value of $(d\mu/d\Delta f)_{\min}$ below T_c^{pw} is presumably due to residual substrate inhomogeneity. Similar analysis has been used previously to identify critical points in 2D liquid-vapor phase transitions [13]. It is remarkable that a step, although progressively rounded, persists in isotherms up to nearly twice the prewetting critical temperature [see, e.g., Fig. 1(a)]. The location of T_c^{pw} divides the curve in Fig. 2 into two parts: For $T_w < T < T_c^{\text{pw}}$, the curve defines the prewetting thick-thin coexistence region, while for $T > T_c^{\text{pw}}$, the curve marks the maximum in the compressibility of the supercritical phase.

Isotherms at temperatures below 1.95 K, as shown in Fig. 1(c), are qualitatively different from those at higher temperature. The frequency shift at saturation Δf_{sat} is an order of magnitude smaller, and there is no indication of a step for $P < P_0$. The way in which nonwetting isotherms below T_w evolve into wetting isotherms above T_w is illustrated in Fig. 4, which shows Δf_{sat} as a function of T. The lowest branch of this curve shows points obtained from the maximum frequency shifts of isotherms taken for a series of increasing temperatures. Care was taken to ensure that bulk liquid covered the bottom of the can at each point. As the temperature approaches T_w from below, the frequency shift at saturation undergoes a nearly discontinuous jump at T_w. This confirms the expectation that T_w is the location of a first-order wetting transition.

First-order transitions are typically hysteretic, and we indeed find that the behavior of the adsorbed film at saturation is completely different, depending on the direction from which T_w is approached. The frequency shift observed for a saturated film prepared above T_w and cooled to low temperatures along the coexistence curve is shown by the upper branch in Fig. 4. The most striking feature of this curve is that it passes through T_w smoothly, and a thick film persists on the substrate far below T_w. For the temperatures of the data in Fig. 4, the thick films are superfluid, and the decrease in Δf_{sat} as the temperature is lowered is not due to thinning of the film, but the fact that the oscillator couples only to the normal fraction of the film, which decreases below 2.17 K. Although the thick film is presumably metastable below T_w, the experimental values of Δf_{sat} are constant for periods up to 10 h. This branch is completely reversible; points taken while warming and cooling retrace the same curve. Note that the hysteresis shown in Fig. 4 is *not* due to capillary condensation, which causes hysteresis in an *isotherm.* The long lifetime of the metastable film is particularly surprising, since the films are superfluid, and chemical potential gradients due to inhomogeneities of temperature, pressure, or film thickness typically relax very quickly via superflow. The thick-to-thin transition cannot, however, take place by a small, continuous redistribution of matter, but rather requires the nucleation of a patch of thin film.

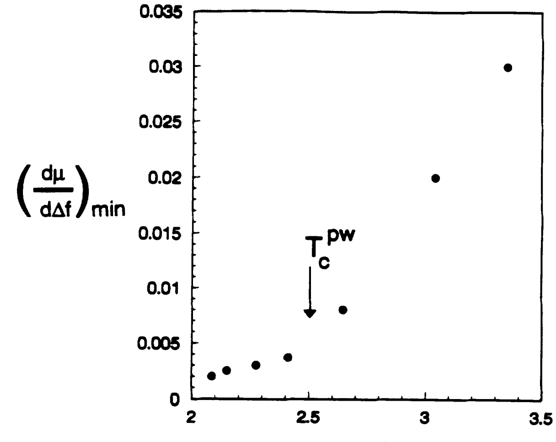

FIG. 3. $(d\mu/d\Delta f)_{\min}$ vs T. The break in slope at 2.5 K identifies the end of the two-phase coexistence region at T_c^{pw}. The small, nearly constant deviations of $(d\mu/d\Delta f)_{\min}$ from zero below 2.5 K result from surface imperfections.

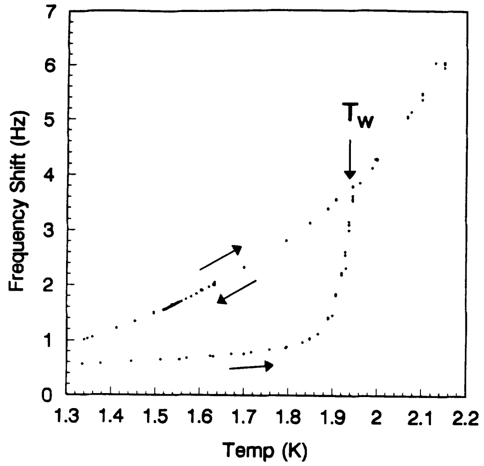

FIG. 4. Δf_{sat} vs T, showing hysteresis in the film. Measurement frequency is 5 MHz. The lower branch corresponds to the small values of Δf_{sat} defined by the top of isotherms for $T < T_w$, such as Fig. 1(c). If the surface is covered by a thick film above T_w and then cooled, a thick, superfluid, metastable film remains on the surface even below T_w, as shown on the upper branch. The slope of the upper branch is due to the variation of the normal fluid fraction with temperature.

The domain wall associated with the patch has an energetic cost proportional to the difference in thickness between the two phases, which is very large below T_w. This accounts for the slow nucleation kinetics and long lifetime of the metastable phase [14].

In summary, helium adsorption on high-quality cesium films displays all of the characteristic features of a first-order wetting transition: a wetting transition temperature T_w, a prewetting line terminating in a prewetting critical point at $T_c^{\rm pw}$, as well as hysteretic behavior below T_w. The phase diagram which we have constructed in Figs. 2 and 4 is the first complete observation of these phenomena in any system [15]. Our results are consistent with the CCST prediction of nonwetting of ^{4}He on cesium at $T=0$, and also with the results of Nacher and Dupont-Roc [2] on optically smooth bulk cesium surfaces at $T=1.3$ K. Even on high-quality surfaces, a thick metastable film will exist far below T_w if the system is cooled along the liquid-vapor coexistence curve. This metastability, which is particularly remarkable since the films are superfluid, leads to hysteresis and can complicate the experimental identification of the wetting transition temperature. Above T_w, there are steps in the isotherms at $P < P_0$ which are clearly visible even at temperatures greater than 4 K. Isotherms above and below $T_c^{\rm pw}$ are qualitatively similar, and identification of the prewetting critical point requires a detailed analysis of the slope of the steps in the isotherms.

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