

## *Rapid Communication*

# Adsorption of $^3\text{He}$ on Cesium Surfaces

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*Vapor pressure isotherms of  $^3\text{He}$  on Cs are reported which show that, in contrast to  $^4\text{He}$ ,  $^3\text{He}$  wets Cs for  $1.26\text{K} < T < 2\text{K}$ . Although the isotherms are distinctly different from those taken on strong binding substrates, we have observed no evidence for a first order prewetting transition. The data suggest that the prewetting critical point is substantially below  $T=1.26\text{K}$ .*

A number of experiments<sup>1</sup> over the last two years have shown that  $^4\text{He}$ <sup>2</sup> and  $\text{H}_2$ <sup>3</sup> display first order wetting transitions<sup>4,5</sup> on the surfaces of the heavy alkali metals. These experiments are of interest for several reasons. Wetting transitions result when the binding of an adsorbate to a substrate is weaker than the binding of the adsorbate to itself. It is therefore surprising that the low temperature quantum liquids display a wetting transition at all, since they have an extremely low cohesive energy. Not only is the binding to the heavy alkali metals weak enough to allow a wetting transition, but the wetting transition of  $^4\text{He}$  on cesium and  $\text{H}_2$  on rubidium display a clear prewetting line. Prewetting, a thermodynamic consequence of first order wetting, had escaped detection in all other wetting experiments for over a decade.<sup>4,5</sup> Finally, the interactions within the adsorbate and between the adsorbate and substrate in the case of He on an alkali metal are relatively simple and can be theoretically analyzed at a fundamental level, so quantitative comparisons between experiment and theory should be possible. Indeed all of the work that has been done on adsorption of light gases on the heavy alkali metals is the result of the theoretical prediction of nonwetting of  $^4\text{He}$  on these surfaces.<sup>1</sup>

In contrast,  $^3\text{He}$  is predicted to wet all known surfaces, including the alkali metals. Although the van der Waals interaction of the two isotopes with the substrate is identical, the increased zero point energy of  $^3\text{He}$  decreases the cohesive energy and the surface tension compared to  $^4\text{He}$ . A simple thermodynamic estimate suggests that the surface tension of  $^3\text{He}$  is sufficiently low to guarantee wetting of the weak binding alkali metals even at  $T=0$ . We report here the first adsorption isotherm studies on the growth of  $^3\text{He}$  on the surface of cesium. Our results show that  $^3\text{He}$  wets a cesium surface well below the wetting temperature of  $^4\text{He}$  on the same surface. Recently Pricauptenko and Treiner<sup>6</sup> have presented a detailed theoretical

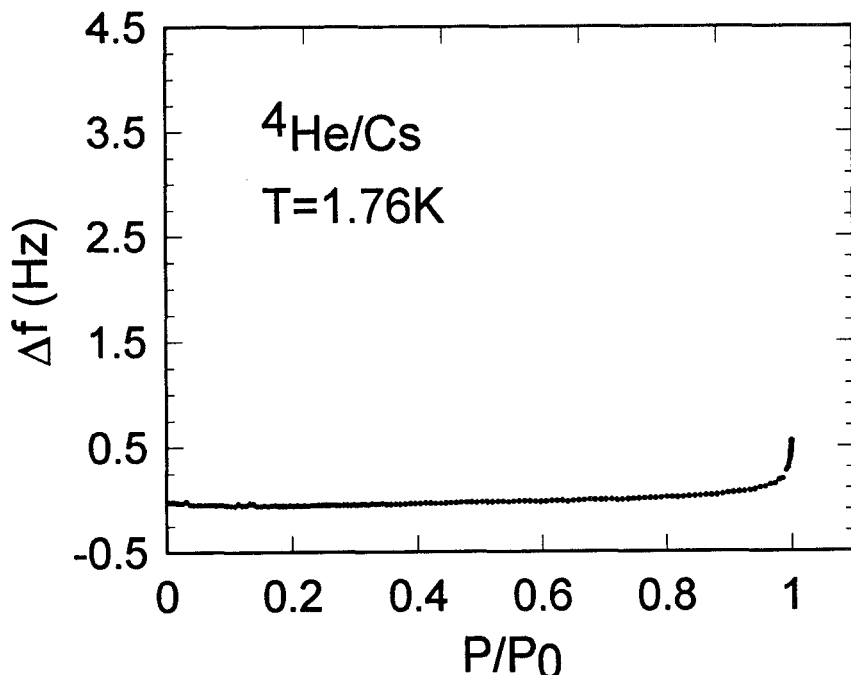


Fig. 1. Frequency shift  $\Delta f$  versus reduced pressure  $P/P_0$  isotherm at  $T=1.76\text{K}$  for  ${}^4\text{He}$  on a cesium substrate with a wetting temperature of  $T_w=2.2\text{K}$ . The frequency shift at the saturated vapor pressure is approximately 0.5 Hz, which corresponds to a coverage of less than three layers.

analysis of the adsorption of  ${}^3\text{He}$  on cesium, potassium and sodium.

Their work predicts that all three substrates are wet by  ${}^3\text{He}$  down to K. In addition, Pricaupenko and Treiner predict that for potassium and cesium, a prewetting transition, or even a series of them, occur as the wetting film approaches bulk co-existence. Within their model, prewetting for  ${}^3\text{He}$  is strongly influenced by Fermi statistics. We present data and an analysis that suggest that prewetting of  ${}^3\text{He}$  on cesium will not occur until the temperature is so low that a classical corresponding states argument no longer applies. Our experiment utilizes a quartz microbalance to measure adsorption isotherms. The techniques are similar to those used in a series of measurements on pure  ${}^4\text{He}$  films.<sup>2,7,8</sup> For these experiments, the cold volume of the apparatus was reduced to approximately  $20\text{cm}^3$  so that saturated vapor pressure could be reached using a few STP liters of  ${}^3\text{He}$ . The cesium films were formed by *in situ* evaporation of pure cesium metal over the mass sensitive regions of a 5.5 MHz quartz microbalance. The experiment consists of fixing the temperature of the microbalance and the vacuum can surrounding it, and monitoring the resonant frequency of the microbalance as a function of pressure,  $P$ , as helium gas is admitted into the vacuum can. After corrections are made for viscous gas loading and the pressure coefficient of the resonant frequency, the frequency shift  $\Delta f$  of the

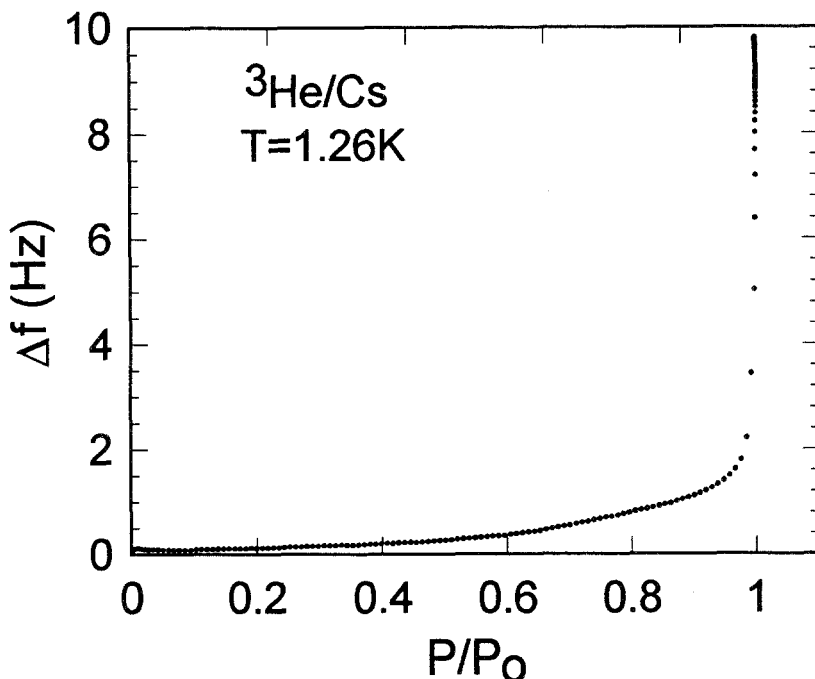


Fig. 2. Frequency shift versus reduced pressure  $P/P_0$  isotherm at  $T=1.26\text{K}$  of  $^3\text{He}$  on the same cesium substrate that was used for the data shown in Figure 1. The rapid increase in adsorbed mass near the saturated vapor pressure  $P_0$  indicates that  $^3\text{He}$  wets cesium at this temperature.

microbalance is proportional to the mass of the adsorbed film.

The sensitivity of the microbalance is 0.24 and 0.15 Hz per monolayer for  $^4\text{He}$  and  $^3\text{He}$ , respectively. The precision of our frequency measurement allows us to detect changes in mass of less than 0.05 monolayers of each gas.

After coating the microbalance with cesium we measured a series of  $^4\text{He}$  isotherms to assess the quality of the cesium film. As described in reference [2], steps in the isotherms were used to locate the prewetting line in the  $P$ - $T$  plane. The extrapolation of the prewetting line to the coexistence curve yielded a value for the wetting temperature of  $T_w = 2.2\text{K}$ . The wetting temperature depends on the cesium evaporation rate and the substrate temperature during the evaporation<sup>8</sup> and is typically between 1.95 K and 2.25 K. We also measured  $^4\text{He}$  isotherms below the wetting temperature. One of these measured at 1.7 K is shown in Fig. 1. The  $\sim 0.5\text{Hz}$  frequency shift, corresponding to about two monolayers at liquid vapor coexistence confirms that  $^4\text{He}$  does not wet the cesium surface at this temperature. Both the wetting temperature and the size of the frequency shift at coexistence for  $T < T_w$  are typical of all the cesium films we have made by this technique.

The distinct difference in the wetting behavior of  $^3\text{He}$  and  $^4\text{He}$  is illustrated

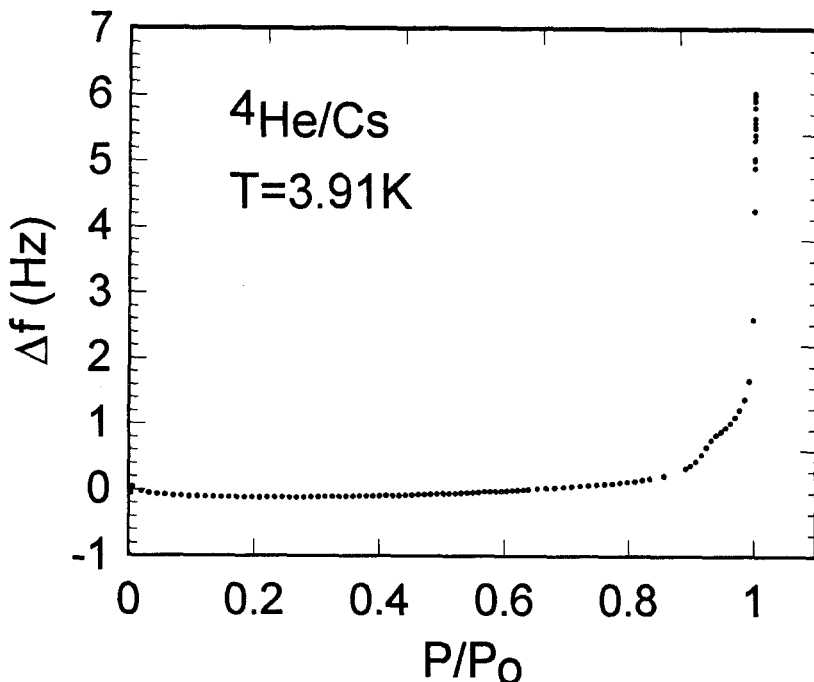


Fig. 3. Frequency shift  $\Delta f$  versus reduced pressure  $P/P_0$  isotherm at  $T=3.91\text{K}$  for  ${}^4\text{He}$  on a cesium substrate with a prewetting critical temperature of  $T_{pw_c}=2.5\text{K}$ . The feature near  $P/P_0 = 0.9$  is due to a maximum in the 2D compressibility which persists far above  $T_c^{pw}$ .

by the data in Figure 2, which shows a  ${}^3\text{He}$  isotherm measured at 1.26 K on the same cesium substrate as was used for the data in Figure 1. The 10 Hz frequency shift at liquid vapor coexistence corresponds to about 70 adsorbed monolayers and shows that the  ${}^3\text{He}$  film wets the surface. This agrees with the simple surface tension model as well as with the detailed calculations of Pricaupenko and Treiner.<sup>6</sup> Although  ${}^3\text{He}$  wets Cs at much lower temperatures than  ${}^4\text{He}$ , it is important to note that the isotherm of Figure 2 is quite different from an isotherm on a conventional strong binding substrate such as gold. (An example of a gold isotherm is shown in Figure 3a in reference 7). In particular, the data of Figure 2 show that the substrate is virtually dry for  $P/P_0 < 0.25$ , and the curvature has the opposite sign of a conventional isotherm. Although the competition between surface tension and the substrate potential favors wetting for  ${}^3\text{He/Cs}$ , the behavior of thin adsorbed films is clearly anomalous.

Another important difference between  ${}^3\text{He}$  and  ${}^4\text{He}$  is the way in which the wet state is approached as the pressure approaches the saturated vapor pressure. For  ${}^4\text{He}$ , our previous work has shown that for all temperatures greater than the wetting temperature, the adsorbed mass versus pressure isotherms always display

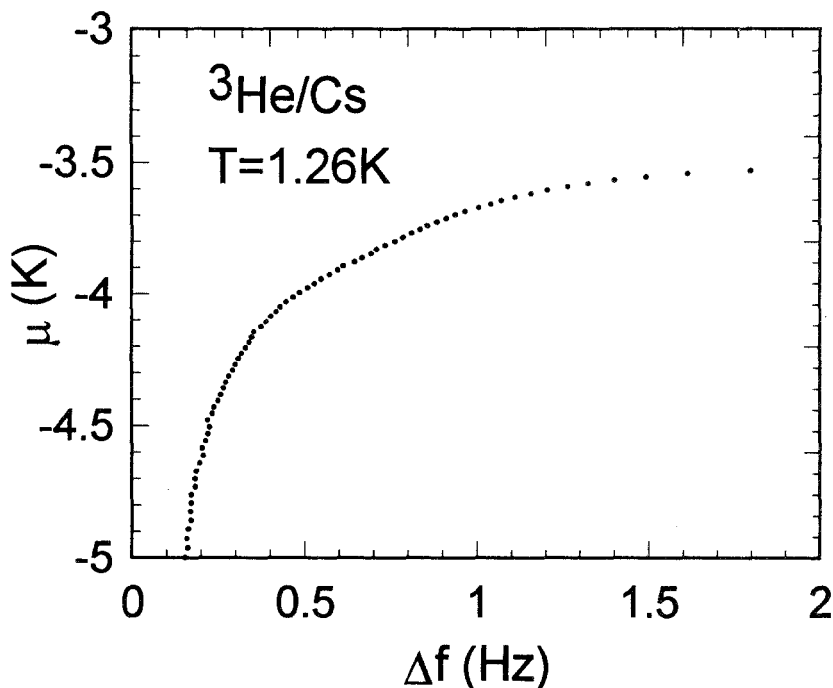


Fig. 4.  $^3\text{He}$  chemical potential  $\mu$  as a function of frequency shift  $\Delta f$  for the same data as shown in Figure 2. The signature of prewetting is a horizontal section of this curve with  $\mu < \mu_{\text{coex}} \approx -3.5\text{K}$ . Although there is no horizontal section in the data, there is slight feature at  $\mu \approx -3.8\text{K}$  where the curvature is low.

a pronounced step corresponding to a rapid variation of the film thickness with pressure. For  $T < T_c^{pw}$ , this step marks the first order prewetting transition between thick and thin surface phases. On an ideal homogeneous substrate, this phase transition would take place at a unique value of the chemical potential, so the step in the isotherm would be vertical. On real surfaces, the prewetting step has a non-zero width, but our previous experience with  $^4\text{He}$  has shown that the pressure typically varies by less than 0.1% of the saturated vapor pressure across the prewetting step, which corresponds to a spread in the chemical potential of approximately 5mK (See Figure 3 of reference 2). For temperatures higher than the prewetting critical point  $T_c^{pw}$ , (which for  $^4\text{He}$  is approximately 2.5K), there is only one surface phase, but we invariably observe steps in the isotherm which differ only subtly from those seen below  $T_c^{pw}$ . These steps mark a locus of maxima in the two dimensional compressibility in the  $P - T$  plane which forms a line that extends from the prewetting critical end point to higher temperature. Even at 3.9 K, the width of the step in the isotherm is only  $\delta\mu = 0.2\text{K}$ , as illustrated in Figure 3.

In contrast to the  $^4\text{He}$  case, in  $^3\text{He}$  the transition from the submonolayer coverage region at low pressure to the thick film region occurs gradually over a wide range

in pressure and chemical potential, as shown in Figure 2. There is no evidence for a prewetting step nor even a feature as prominent as the enhanced compressibility feature at 3.9 K seen for  $^4\text{He}$ . In Figure 4, we show the same data as in Figure 2 in the  $\mu - \Delta f$  plane for comparison with theoretical  $\mu$  versus  $N$  plots at  $T=0$  presented by Pricapenko and Treiner.<sup>6</sup> There is a broad feature with  $\delta\mu \approx 0.5\text{K}$  in the isotherm in the vicinity of  $P/P_0=0.8$ , corresponding to  $\mu \approx -3.8\text{K}$ , which may in fact be the high compressibility remnant of prewetting well above the critical temperature.

The prewetting critical temperature can be determined experimentally by analyzing the temperature dependence of the width of the step in the isotherm, which can be quantitatively characterized by the minimum value of  $(\frac{d\mu}{d\Delta f})$ . For  $T > T_c^{pw}$ , the width of the high compressibility region is approximately linear in the temperature. The high temperature data can be extrapolated to find the value of  $T$  at which the width vanishes, which defines  $T_c^{pw}$ . This type of analysis was carried out for  $^4\text{He}$  in reference 2, but our present apparatus is restricted to temperatures above 1.2K, so it was impossible to repeat this procedure for  $^3\text{He}$ . We are presently constructing an apparatus to allow us to perform these measurements at low temperatures.

We can nevertheless make a rough estimate of  $T_c^{pw}$  for  $^3\text{He}$  based on the fact that a plot of  $(\frac{d\mu}{d\Delta f})_{min}$  vs.  $T$  is linear with a slope that can be estimated using a corresponding states argument. Figure 3 of reference 2 shows a plot of  $(\frac{d\mu_4}{d\Delta f})_{min}$  as a function of temperature for  $^4\text{He}$ . The slope is related to thermodynamic quantities using the relation  $\frac{d\mu}{dT} = (\gamma^2 \kappa_T)^{-1}$ , where  $\gamma$  is the coverage, and  $\kappa_T$  is the 2D isothermal compressibility. In the vicinity of  $T_c^{pw}$ , the mean field behavior of the compressibility is  $\kappa_T = \kappa_0(T - T_c^{pw})^{-1}$ , where  $\kappa_0$  is a material dependent constant. The linear behavior of the data in Figure 3 of reference 2 above  $(T - T_c^{pw})$  justifies the mean field approximation and shows that

$$\frac{d\mu_4}{d\Delta f} = B_4(T - T_c^{pw}) \quad (1)$$

has a wide range of validity for  $^4\text{He}$ , with  $B_4 \sim (\gamma^2 \kappa_{40})^{-1} = 0.035 \frac{K}{Hz}$ . We expect that a similar equation, but with a coefficient  $B_3 \sim (\gamma^2 \kappa_{30})^{-1}$  is valid for  $^3\text{He}$ . Since compressibility scales inversely as the critical pressure, we expect that  $B_3 \approx \frac{B_4}{2}$ . If we use a value of  $(\frac{d\mu_3}{d\Delta f})_{min} = 0.5 \frac{K}{Hz}$  for the data in Fig. 4, and attempt to fit it to an equation of the form of Eq. 1, we find that the predicted value of  $T_c^{pw}$  is negative. Even if our estimate of  $B_3$  is too low by a factor of 30, which we consider unlikely, the predicted value of  $T_c^{pw}$  remains less than zero. This argument ignores statistics, and becomes invalid when the temperature is a fraction of the degeneracy temperature of the adsorbed  $^3\text{He}$ . We conclude that in the temperature range above 1K where the liquid is essentially classical,  $^3\text{He}$  is far above its prewetting critical point, and that prewetting could occur only below 0.3K when the effects of degeneracy become important.

Our experimental results show that the prewetting critical temperature for  $^3\text{He}$  on Cs is less than 1.26K and is possibly equal to zero. The experimental confirmation of prewetting in adsorbed films of  $^3\text{He}$  will require experiments at temperatures considerably below 1 K.

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