

Triple Point Dewetting Transitions of Helium Mixtures on Cesium

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The adsorption of ^3He - ^4He mixtures on a cesium substrate has been measured near bulk liquid phase separation. A first order wetting transition is found on the bulk three phase coexistence line at $T_w \cong 0.53$ K. The ^3He rich liquid phase wets the surface below T_w , and layered films of ^4He rich liquid under a ^3He rich layer wet the substrate above T_w . The surface phase transition line associated with this wetting transition is found to extend to both sides of the bulk coexistence line. On the ^4He rich side it becomes a line of triple point induced dewetting transitions.

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Over the last several years, liquid helium has become an important system for the study of wetting [1]. In particular, studies of pure ^4He adsorption on cesium resulted in the first measurements of the complete phase diagram associated with a first order wetting transition [2]. The experiment reported in this Letter examines the wetting behavior of ^3He - ^4He mixtures on cesium near the bulk phase separation line. It provides the first direct observations of triple point dewetting transitions and reveals a connection between wetting, prewetting, and triple point dewetting transitions that should be a general feature of binary liquid wetting.

Wetting transitions result from the competition of bulk phases to minimize their free energies by interacting with a substrate. In a single component system, such as pure ^4He , wetting occurs at the coexistence between two bulk phases. In two component systems three bulk phases can coexist and the wetting behavior is correspondingly richer [3].

Figure 1 is a sketch of the familiar T vs X_3 phase diagram for liquid helium mixtures, where X_3 is the concentration of ^3He in the bulk liquid. The region underneath the bold solid curve is the region of bulk phase separated liquid. For the bulk liquid at saturated vapor pressure, this is a region of bulk three phase coexistence: ^3He rich "concentrated" liquid (C), ^4He rich "dilute" liquid (D), and saturated vapor (SV). When the phase diagram is plotted in temperature-chemical potential space, this region becomes a line, and so it will be referred to in this Letter as the bulk triple line. Our experiment explores the wetting behavior of helium mixtures on cesium substrates near the triple line. In this case three bulk phases D , C , and SV compete for access to the substrate.

On typical substrates, the strongly attractive van der Waals potential dominates the thermodynamics. A layer of the denser D liquid is always found near the substrate, even on the high concentration side of the triple line in Fig. 1. The strong van der Waals binding more than compensates the thermodynamic costs of stabilizing the D liquid and creating the interface between D and C [4]. For weakly attractive substrates such as cesium, the van der Waals energy and the energy required to create

a D/C interface are comparable. Pettersen and Saam [5] have explored the weak binding case and made detailed predictions of the wetting behavior expected for helium mixtures on Cs, and some experimental investigations of this system have been done [6-8].

This Letter reports the measurement of phase transitions in helium mixture films on cesium. The locations of the film phase transitions are shown as dashed lines in Fig. 1. Along the bulk triple line, the substrate is always covered with a thick film of liquid. However, there is a first order wetting transition within the film at $T_w \cong 0.53$ K. Below T_w , on the triple line, a thick film of concentrated liquid covers the surface. Above T_w , on the triple line, a thick layer of dilute liquid forms between the concentrated liquid and the substrate, so that the adsorbed film contains both liquid phases. The prewetting line associated with this wetting transition is found to extend upward from T_w on the ^3He rich side of the triple line.

In addition, a line of surface phase transitions, labeled as the dewetting line in Fig. 1, is found extending downward from T_w on the dilute side of the triple line.

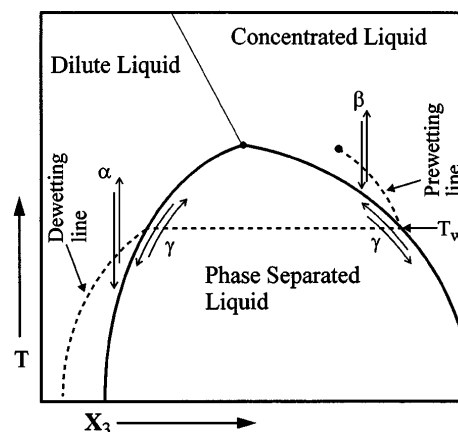


FIG. 1. The T vs X_3 phase diagram for helium mixtures on cesium. For clarity, the phase diagram is not drawn to scale. The bulk three phase region is the region beneath the bold solid line. The dashed lines indicate phase transitions in the adsorbed film. The arrows marked α , β , and γ indicate trajectories taken in the experiment.

Between this dewetting line and the bulk triple line a film of C covers the cesium. However, in this region the C liquid is unstable in the bulk, so the C film cannot be macroscopically thick, and therefore the cesium surface is nonwet. Since this dewetting line marks the coexistence of thick wetting films at high temperatures, and nonwet films at lower temperatures, it is a line of triple point induced dewetting transitions [9,10]. Triple point dewetting was predicted to occur in this system by Pettersen and Saam [5].

Our experimental techniques are similar to those we used to study adsorption in other systems and have been described previously [2]. The experimental apparatus consists of a vacuum can with a cesium coated quartz microbalance mounted near the top. A bulk ^3He - ^4He liquid mixture fills the bottom of the can. Under these conditions a film of liquid is adsorbed onto the microbalance causing a shift, Δf , of the resonant frequency relative to its value in vacuum. The sensitivity of the microbalance is approximately 0.133 Hz/monolayer of liquid ^3He . The microbalance oscillates in a shear mode, so it is insensitive to the superfluid component of the films. In the temperature range of this experiment, virtually all of the ^4He in the dilute liquid phase is superfluid, so $-\Delta f$ is essentially a measure of the ^3He content of the films. The microbalance is typically located ~ 3 cm above the surface of the liquid, so the gravitationally limited thickness of the adsorbed films is always much less than the viscous penetration depth for the frequency used (5.5 MHz).

Our results consist of measurements of $-\Delta f$ as a function of the coordinates on the phase diagram of Fig. 1 [11]. Two types of trajectories were taken through the phase diagram: constant X_3 trajectories on both the dilute and concentrated sides of the bulk triple line, labeled α and β in Fig. 1, and trajectories along the bulk triple line, labeled γ . Care was taken to ensure that the liquid was well mixed and equilibrated before each run was started, and that a sufficient quantity of liquid was present so that the fraction of helium atoms in the vapor was always less than 5×10^{-3} of the total, so that X_3 is constant along the α and β trajectories to within 0.003.

The data taken for ^3He concentrations on the dilute side of the bulk triple line are plotted as the top four curves of Fig. 2. For clarity, the data sets for each concentration are shifted vertically with respect to each other, and plotted as a function of $T - T_s$, where T_s is the bulk triple line temperature for that concentration. These data were taken on trajectories like the one marked α in Fig. 1. At the highest temperatures for each mixture, far from the bulk triple line, previous experiments [6–8] and the behavior of the films as they were cooled from ~ 4 K indicate that the substrate was wet by a thick superfluid D film covered by a layer of C [12]. As the temperature was lowered toward T_s the mass of the film increased slightly as the C layer on top became thicker. This trend continued until a point, near but still above T_s , where there was a

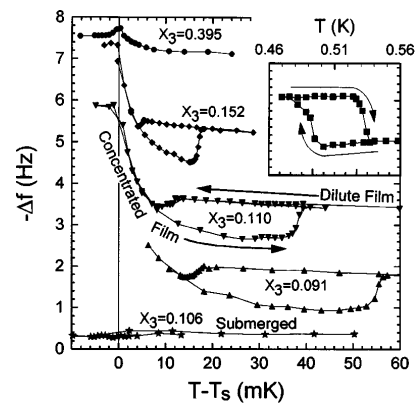


FIG. 2. Triple point dewetting measurements taken on trajectories like the one marked α of Fig. 1. The dewetting transitions are hysteretic so that the surface is dewet and rewet by the dilute liquid at different temperatures, forming the loops in the data. The bottom curve was measured with the substrate submerged within the liquid rather than suspended above it. The inset graph is data from a measurement along the bulk triple line, showing the first order wetting transition with $T_w \cong 0.53$ K. Above this temperature the dilute liquid wets the concentrated liquid-cesium interface; below, it does not.

sharp drop in the ^3He content of the films. As cooling continued, the frequency shift indicated a rapid increase of the film ^3He content as the temperature approached T_s . For $T \leq T_s$, $-\Delta f$ became nearly constant. When the direction of the temperature sweeps was reversed, the behavior of the adsorbed films was found to be hysteretic. The observed hysteresis loops are clear signatures of a first order phase transition in the adsorbed films.

Because the concentrated layer on top of a dilute film is known to evolve smoothly [12], the observed phase transitions cannot be a thinning of that part of the film. There are two possible explanations for these phase transitions: a first order transition that occurs at the interface between the dilute film and the substrate, or a thinning of the dilute film. To distinguish between these two possibilities, we repeated the measurement with the microbalance submerged within the dilute liquid rather than suspended above it [13]. If the observed transitions in the films had occurred at the dilute-cesium interface, they would be unaffected by the immersion of the substrate. If, however, the transitions were a thinning of the film, they could not occur on the submerged substrate. The bottom curve of Fig. 2 shows the results of this measurement. No transition occurred.

The observed phase transitions are therefore between thick wetting dilute liquid films at high temperatures and thinner nonwetting films at low temperature. They are triple point induced dewetting transitions [9,10]. At these phase transitions, films with a structure $\text{Cs}/D/C/SV$ have the same free energy and therefore coexist with films having a $\text{Cs}/C/SV$ structure. Above the phase transition the $\text{Cs}/D/C/SV$ films have the lowest free energy and are the equilibrium phase. This phase is known to wet Cs

substrates [6–8], and is qualitatively the same phase that wets strong substrates in this region of the bulk phase diagram. Below the transition, the situation reverses and the Cs/C/SV structure is stabilized. In the region between the film phase transition and the bulk triple line, the bulk *C* liquid is thermodynamically unstable and only a microscopic film of it can exist. Thus moving across the transition from high to low temperature the film undergoes a transition from wet to nonwet. The interplay between the van der Waals potential, the surface tensions, and the costs of stabilizing liquids that are unstable in bulk determines the thicknesses of the liquid layers as is described by Pettersen and Saam [5,14].

As can be seen in Fig. 2, for successively richer ^3He mixtures the dewetting transitions move monotonically closer to T_s , until finally for the $X_3 = 0.395$ solution no transition was observed, indicating that the line of dewetting transitions intersected the bulk triple line. To locate this intersection, a mixture was cooled below T_s so that the experimental trajectory, labeled γ in Fig. 1, followed the bulk triple line. These data are shown in the inset graph of Fig. 2. At high temperatures the mass of ^3He in the film is small and there is a first order hysteretic phase transition to a film with a larger ^3He content at lower temperatures.

This phase transition along the bulk triple line has a second, equivalent, description. On the low temperature side the surface is covered by a macroscopic film of *C*. As the temperature is warmed through the transition point, a thick layer of *D* abruptly forms between the concentrated liquid and the substrate. Seen this way the transition is a first order wetting transition of the dilute liquid at the Cs/*C* interface, with a wetting temperature $T_w \cong 0.53$ K.

First order wetting transitions are accompanied by prewetting transitions [15,16]. In this case, the prewetting line should extend upward in temperature from T_w , on the ^3He rich side of the bulk triple line. Figure 3 shows the data for the measurements of this prewetting line. For temperatures far above T_s , the substrate was wet by a thick film of concentrated liquid. As the experiment was cooled toward T_s , a sharp break in the slope of the curves was found. These abrupt changes in slope of the data of Fig. 3 locate the prewetting transitions between concentrated films at high temperatures and *C* films with a layer of *D* at the substrate at low temperatures. The $X_3 = 0.873$ prewetting transition was hysteretic, though its width, 0.6 mK, was much smaller than that of the dewetting transitions. The prewetting transitions moved monotonically closer to T_s as the ^3He concentration was increased until the prewetting line intersected the bulk triple line at $T = T_w$. For the $X_3 = 0.905$ mixture, $T_s < T_w$, so no transition occurred.

Figure 4 shows the locations of the surface phase transitions measured for this system. In order to show the relationship between the prewetting and dewetting lines clearly, the bulk three phase region of Fig. 1 has been com-

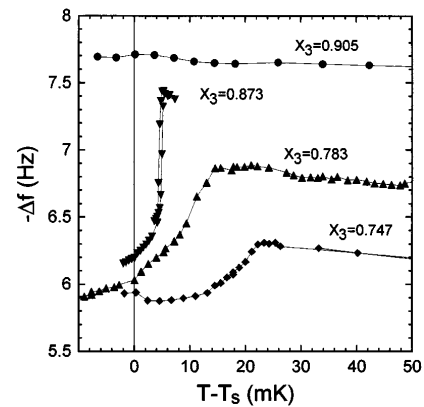


FIG. 3. Prewetting line measurements taken on trajectories like the one marked β of Fig. 1. At high temperatures, a thick concentrated liquid film covers the substrate. Closer to T_s , a layer of dilute liquid forms between the surface and the concentrated liquid. The growth of this dilute layer occurs in a steep jump at the prewetting transition.

pressed into a line by plotting the dewetting transition temperatures vs $X_3^{sd}(T) - X_3$, and the prewetting transitions vs $X_3 - X_3^{sc}(T)$, where $X_3^{sd}(T)$ and $X_3^{sc}(T)$ are the ^3He concentrations of the coexisting dilute and concentrated liquids on the bulk triple line at temperature T . Because the cesium film forms an island on the strongly adsorbing quartz surface of the microbalance, a dilute layer is always present in the film at the edges of the cesium. As a result, transitions to dilute films on the cesium are nucleated at the edges, and concentrated films are not metastable in this experiment. The concentrated film branches of the measured

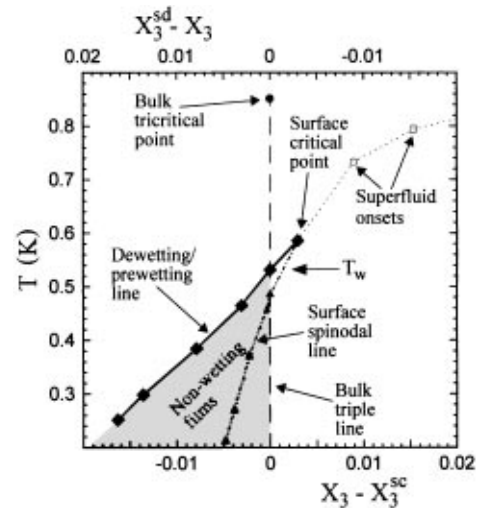


FIG. 4. The dewetting-prewetting line. For clarity, the three phase coexistence region of Fig. 1 is compressed into a line by plotting the transition temperatures vs $X_3^{sd}(T) - X_3$ and $X_3 - X_3^{sc}(T)$. Below and to the right of the dewetting-prewetting line, films of concentrated liquid cover the surface. Above and to the left of the line, films with a layer of concentrated liquid on top of a dilute liquid layer are adsorbed. Plotting the data in this way is qualitatively similar to plotting the transition temperatures vs the chemical potential difference.

hysteresis loops are therefore the thermodynamically stable ones. For this reason, the actual phase transition temperatures are at the concentrated \rightarrow dilute end points of each of the hysteresis loops (the high temperature end points in Fig. 2). The opposite end points of the hysteresis loops are plotted as the spinodal line. Extrapolation of this spinodal line to its intersection with the prewetting line gives an estimate for the critical end point of the surface coexistence line at $T_{\text{surf}}^c \cong 0.59$ K. Above the surface critical point the phase transitions in the film are no longer first order, but a remnant of the prewetting transitions persists at which a layer of superfluid forms at the cesium substrate.

Figure 4 clearly shows that the dewetting and prewetting lines intersect with the bulk triple line at the same point, and are actually different manifestations of the same surface phase transition. This dewetting-prewetting line is the coexistence line between two qualitatively different kinds of adsorbed films. To the right and below the line, films of concentrated liquid are adsorbed. To the left and above the line, films with dilute liquid at the substrate and concentrated liquid on top are adsorbed.

The wetting transition and its associated prewetting line on the right side of Fig. 4 form the usual phase diagram of a first order wetting transition, examples of which have been found recently in several experiments [2,17,18]. The extension of the surface phase transition as a dewetting line on the other side of the bulk triple line, however, has not been previously observed. Previous experiments have studied either systems of only two coexisting bulk phases [2,6,18] or the wetting of one bulk phase at the interface between two others [17]. The experiment reported here differs from previous work in that it examines a wetting transition at a substrate along a bulk three phase coexistence line. It is the presence of the third bulk phase, the vapor in this experiment, that causes the prewetting line to cross the bulk coexistence line and become a triple point dewetting line. The dewetting-prewetting line found in this experiment should be a general feature of the wetting of a broad class of binary liquid mixtures.

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[1] E. Cheng *et al.*, *Rev. Mod. Phys.* **65**, 557 (1993).

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

- [3] See, for example, S. Dietrich and M. Schick, *Phys. Rev. B* **33**, 4952 (1986).
- [4] J.P. Romagnan *et al.*, *J. Low Temp. Phys.* **30**, 425 (1978).
- [5] M.S. Pettersen and W.F. Saam, *Phys. Rev. B* **51**, 15 369 (1995).
- [6] K.S. Ketola and R.B. Hallock, *Phys. Rev. Lett.* **71**, 3295 (1993).
- [7] D. Ross, P. Taborek, and J.E. Rutledge, *Phys. Rev. Lett.* **74**, 4483 (1995).
- [8] K.S. Ketola, T.A. Moreau, and R.B. Hallock, *J. Low Temp. Phys.* **101**, 343 (1995).
- [9] R. Pandit and M.E. Fisher, *Phys. Rev. Lett.* **51**, 1772 (1983).
- [10] M.S. Pettersen, M.J. Lysek, and D.L. Goodstein, *Phys. Rev. B* **40**, 4938 (1989).
- [11] Thermodynamically T and X_3 , the ^3He concentration in the bulk liquid, completely specify the state of the system. Therefore, any difference between X_3 and the ^3He concentration in the film is irrelevant to a thermodynamic study of wetting.
- [12] D.O. Edwards and W.F. Saam, in *Progress in Low Temperature Physics*, edited by D.F. Brewer (North-Holland, New York, 1978), Vol. VIIa, Chap. 4.
- [13] In this arrangement, although there is a first order phase transition in the bulk liquid surrounding the microbalance, the ^3He concentration is a continuous function of temperature.
- [14] The low temperature behavior we have found is essentially identical to that predicted in Ref. [5]. Quantitatively we estimate that the zero temperature dewetting transition occurs at $X_3 = 0.048 \pm 0.003$ whereas the prediction is $X_3 = 0.052$. At higher temperatures the topology of the measured phase transition differs from the prediction. The dewetting line is predicted to end at the bulk tricritical point. In contrast, we have determined that it intersects the triple line at $T_w = 0.53$ K with a corresponding prewetting line in the C region terminating in a distinct surface critical point. The discrepancy stems from the fact that the second term on the left hand side of Eq. (32) in Ref. [7] is in fact negative. With this realization the Pettersen and Saam model [5] predicts the same qualitative finite temperature topology we have observed.
- [15] J.W. Cahn, *J. Chem. Phys.* **66**, 3667 (1977).
- [16] C. Ebner and W.F. Saam, *Phys. Rev. Lett.* **38**, 1486 (1977).
- [17] See, for example, H. Kellay, D. Bonn, and J. Meunier, *Phys. Rev. Lett.* **71**, 2607 (1993).
- [18] G. Mistura, H.C. Lee, and M.H.W. Chan, *J. Low Temp. Phys.* **96**, 221 (1994).