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## Contact Angle of Superfluid Helium Droplets on a Cesium Surface

D. Ross, P. Taborek and J.E. Rutledge

Department of Physics and Astronomy, University of California, Irvine, CA.  
92697-4575, USA

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*We present pictures of superfluid drops on several cesium surfaces prepared in different ways. These pictures are used to determine the temperature dependence of the contact angle. The results show that the temperature dependence of the helium-cesium surface tensions depends on the wetting temperature. The relationship between these results and other recent measurements of the temperature dependence of the contact angle is discussed.*

### 1. INTRODUCTION

In recent years the study of the adsorption of quantum liquids on alkali metal substrates has resulted in a great deal of progress in the understanding of wetting phenomena. In particular, the prediction that  $^4\text{He}$  would not wet cesium at low temperatures<sup>1</sup> led to the observation of a wetting transition of a simple liquid on a solid substrate and the first measurements of a prewetting line in any system<sup>2</sup>. Further experimental efforts resulted in the first observations of phenomena such as reentrant wetting<sup>3,4</sup> and triple point induced dewetting<sup>5</sup>.

The wetting properties of a liquid are determined by surface tensions. If a droplet of liquid is placed on a surface which it does not wet, the contact angle of the edge of the drop is related to the surface tensions of the system through Young's equation<sup>6</sup>:

$$\sigma_{lv}\cos\theta = \sigma_{sv} - \sigma_{sl} \equiv \Delta\sigma, \quad (1)$$

where  $\theta$  is the contact angle, and  $\sigma_{lv}$ ,  $\sigma_{sv}$ , and  $\sigma_{sl}$  are the surface tensions of the liquid-vapor, substrate-vapor, and substrate-liquid interfaces, respec-

tively. At the wetting temperature,  $T_w$ , the contact angle goes to zero and the droplet will spread into a wetting film on the surface. Thus the contact angle gives insight into the fundamental thermodynamic quantities that determine wetting properties.

At present there are two measurements of the temperature dependence of the contact angle of  $^4\text{He}$  on Cs due to Klier et al.<sup>7</sup> and Rolley and Guthmann<sup>8</sup>. These experiments used different techniques to prepare the cesium surfaces as well as different techniques to measure the contact angle. The results of these two experiments are not in good agreement and the discrepancy has important implications for models of the excitations at the helium-Cs interface. We have constructed an optical cryostat which allows us to image the droplets<sup>9</sup> directly and to determine the contact angle. Cs surfaces prepared in different ways have different wetting temperatures. We find that the temperature dependence of  $\Delta\sigma$  depends on the wetting temperature.

## 2. APPARATUS AND SAMPLE PREPARATION

The apparatus is shown schematically in Fig. 1. The experiment cell and radiation shields are made of OFHC copper and electroplated with gold. A quartz crystal microbalance was used as the substrate. The microbalance could be rotated about a horizontal axis so that both sides could be covered with Cs. Typically Cs was evaporated onto the substrate from a source of pure metal to a thickness of at least 40 monolayers.

In order to assess the effect of surface morphology, we made contact angle measurements on several surfaces prepared under different conditions. During all evaporations, the substrate was held near 6K, except for Surface 2 which was evaporated on an 80 K substrate. During the evaporations, the sample chamber was maintained below 20 K in order to prevent contamination of the highly reactive Cs substrate. During the evaporations of all surfaces except Surface 3, the Cs flux was directed perpendicularly on to the substrate at a rate of 0.01 layers per second. Surface 3 was tipped at an angle of approximately  $40^\circ$ , so that the evaporation rate was about 25% slower. We have also prepared surfaces near 6 K and then annealed them near 80 K for about 30 minutes. The contact angle measurements on these surfaces are identical within the scatter of the data to those on Surface 2, deposited on an 80 K substrate. Therefore we will not explicitly show those results here.

Finally, the gold electrodes onto which the cesium was evaporated were prepared in different ways. For Surfaces 1 and 3, the electrodes were prepared by the microbalance manufacturer. In those cases, a layer of chromium is

preplated under the gold. For Surface 2 and several of the annealed surfaces we evaporated gold directly onto bare quartz. The evaporation was done under near UHV conditions while the substrate was held near 500 K. An STM examination shows that similarly evaporated gold surfaces are smoother than those received from the manufacturer. As received from the manufacturer, the gold films were polycrystalline with a typical grain size of 30nm. The films we evaporated were polycrystalline with a typical grain size of 140nm. It is unclear whether the change in crystallite size is due to differences in the gold evaporation procedure or the presence of a chromium underlayer on the samples from the manufacturer. In any case no qualitative differences in the adsorption behavior on the differently prepared gold surfaces were evident. Our apparatus allows optical inspection of the Cs surfaces we prepared. We were able to view objects and their reflections from the Cs surface with a microscope and digital camera with a combined magnification of 100X. The edges of the objects and their reflections were equally sharp. The Cs surfaces were free of all but a few isolated point defects, mainly dust grains with a typical density of 5 grains  $\text{cm}^{-2}$ . As we did not analyze any cases where the contact line was near a visible defect, they affected none of the results shown here.

### 3. EXPERIMENTAL RESULTS

In order to verify the quality of our Cs surfaces and to provide an independent measure of  $T_w$ , we studied the adsorption characteristics of  $^4\text{He}$  on these surfaces using the microbalance. The bottom of the cell was filled with bulk liquid  $^4\text{He}$  at approximately 1.2 K. At liquid-vapor coexistence and low temperature, the  $^4\text{He}$  adsorbed on the cesiated surfaces of the microbalance was less than 1 monolayer thick indicating that the surface was non-wet. The cell was gradually warmed until the wetting temperature was reached, indicated by an abrupt thickening of the film. The thickening takes place over a range of temperatures ( $< 0.2\text{K}$ ). We identified the wetting temperature as the high temperature limit of this temperature range, where the film reaches its full, gravity limited, thickness. The temperature broadening of the wetting transition is not understood. If surface heterogeneity is the cause, it is reasonable to believe that the wetting temperature we determine is the temperature at which the weakest patches wet. Annealed films and films prepared at high temperatures have wetting temperatures about 0.2 K colder than unannealed films and details of the temperature dependence of the adsorbed mass near  $T_w$  are different. The films studied here are typical of those that have been made in this laboratory<sup>2,5,9-13</sup> over the last several years.

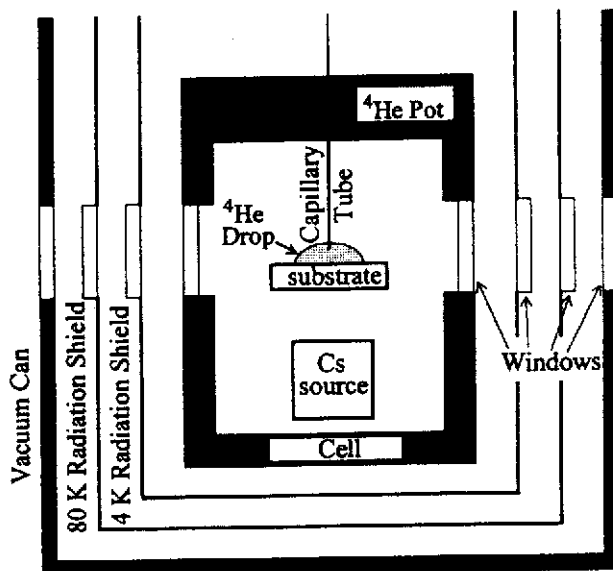


Fig. 1. Schematic diagram of the cryostat. The substrate ( a quartz microbalance) could be rotated about an axis perpendicular to the page to cover both sides with a cesium film. Helium drops were formed on the substrate by adding liquid through a capillary which could be brought to within a fraction of a millimeter of the surface. The helium droplets were observed through one set of windows while they were illuminated through the opposite set.

to the cell through a long thin capillary. These  $^3\text{He}$  levels have negligible effect on the surface tension in the temperature range of our experiment. Potential contaminants of other chemical species would freeze on the capillary wall and not reach the cell. With the end of the capillary very close to the substrate, a drop of liquid could be formed bridging the gap between the capillary and the substrate. This was done so that liquid could be both added to and removed from the droplet in a controlled manner. Figure 2 shows images of droplets of  $^4\text{He}$  on a Cs substrate (Surface 1) at three different temperatures. The 0.04 cm diameter capillary can be seen emerging from the top of the drop. Notice that the contact angle on the capillary is zero, indicating that  $^4\text{He}$  wets its surface. The images in Fig. 2 are taken with a digital camera and a long focal length microscope. The optical axis of the microscope makes a glancing angle with the Cs surface. As the films are specular mirrors, the capillary tube and droplet and their reflections in

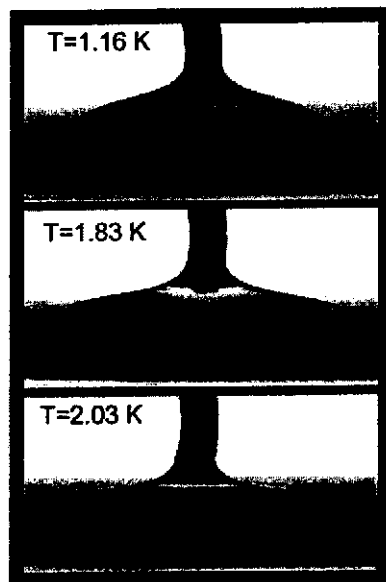


Fig. 2. Microscope images showing an edge-on view of  $^4\text{He}$  drops on a cesiated surface (Surface 1) at three different temperatures. The dark cylinder at the top of each frame is the capillary tube through which helium was added to the drop. The pictures show the outline of the drop as well as its mirror image in the reflective substrate. In each case, the volume of the drop is increasing and the contact line is advancing.

the surface are clearly visible. The sharp points formed by the top surface of the droplet and its reflection mark the plane of the substrate. The focal plane of the microscope contains the capillary tube and the diameter of the drop.

Digitized images like those in Fig. 2 were analyzed to determine the contact angle. An edge finding routine was used to find the coordinates of the edge of the drop which were then fit to a polynomial. The slope of the fit at the contact point determined the contact angle. This method for measuring contact angles is straight-forward and well established<sup>15</sup>. The uncertainty in the contact angles reported here are  $\sim 1^\circ$ .

Although the equilibrium contact angle is a well defined thermodynamic quantity, measured contact angles are generally hysteretic and depend on whether the contact line is advancing or receding. Numerous studies of these effects have shown that for relatively homogeneous surfaces the advancing contact angle is a good measure of the equilibrium contact angle on the

weakest binding regions of the substrate<sup>15</sup>. The images in Fig. 2 were taken while the size of the drop was slowly expanding so the contact angle seen is the advancing contact angle. The contact angle was independent of the velocity of the contact line for the velocities we used.

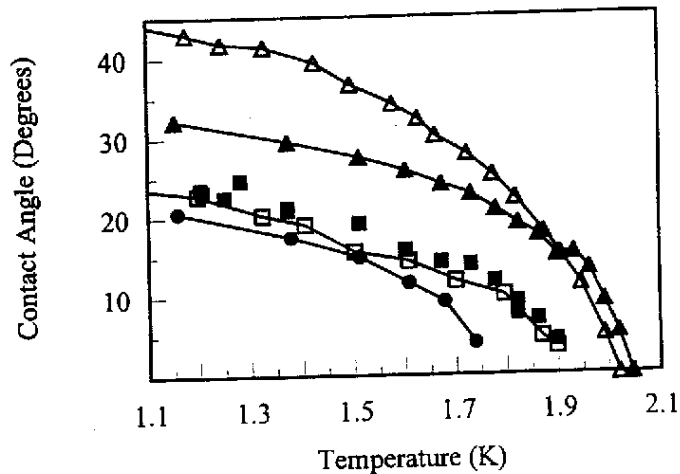


Fig. 3. Contact angle vs. Temperature. The solid triangles, squares, and circles are the data taken with Surfaces 1,2 and 3 respectively. Open squares are data from Ref. 8, open triangles are from Ref. 7

Several precautions were taken to avoid perturbing the droplets with the illumination. The windows attached to the radiation shields were made of infrared absorbing glass. By lighting the drops from behind so that the camera collected transmitted rather than the weaker reflected light, the lighting level could be kept low to avoid heating of the substrate and the droplets. Because the work function of Cs is small (equivalent to  $\sim 690$  nm light), additional filtering was used to cut out the short wavelength components of the light. It is not clear that this precaution mattered as we have not seen effects due to the lighting under any circumstances other than gross over illumination. To verify that all optical perturbations were negligible, images of expanding droplets were taken using a camera flash filtered with a sharp cutoff (at 700 nm) filter. Because of the extremely low total energy, these images were noisier, but the advancing contact angles were found to

be identical within the experimental resolution ( $\pm 1^\circ$ ) to those obtained with the cw light source.

The advancing contact angles measured on all three surfaces are plotted vs. temperature in Fig. 3. Data on Surfaces 1, 2 and 3 are shown as solid triangles, squares and circles, respectively. For each surface, the advancing contact angle has a relatively large value at low temperatures and goes to zero at the same wetting temperature as determined by the microbalance experiments. This agreement is supportive of the assumption that the advancing contact angle is equal to the equilibrium contact angle on the most weakly attractive portions of the surface.

Also shown in Fig. 3 are the results of two other contact angle measurements for the  $^4\text{He}/\text{Cs}$  system. The open squares are the data of Rolley and Guthmann<sup>8</sup>. Their surfaces were made by evaporation from a Cs getter source and the contact angles were determined by interferometrically measuring the liquid depth profile near the contact line on a Cs covered substrate immersed in liquid  $^4\text{He}$ . The open triangles are the data of Klier et al<sup>7</sup>. Their Cs surfaces were formed near room temperature under UHV conditions. Contact angles were inferred from the force exerted on the surface of the liquid by vertical, cesium-covered tungsten plates. The temperature dependence of the contact angles and the wetting temperatures we measured on Surface 2 are nearly identical to those measured by Rolley and Guthmann. It is interesting to note that Rolley and Guthmann report no difference between Cs films prepared on substrates held at 15 K and 70K. In our experiments, films prepared near 80K and near 6K have different wetting temperatures.

The data in Figure 3 can be recast into plots of  $\Delta\sigma$ , defined in Eq. 1, as a function of temperature. Figure 4 shows our results on Surfaces 1, 2, 3 shown as solid triangles, squares and circles, the same correspondence as in Fig. 3. The systematic trend in our data is also evident here. On Cs surfaces with higher wetting temperatures, the temperature dependence of  $\Delta\sigma$  is stronger. Included in the Figure are the results from References 7 and 8. The data in Reference 8 are nearly identical to our Surface 2 data. The temperature dependence of  $\Delta\sigma$  from Reference 7 is markedly stronger than is seen in any of the other experiments and is markedly different from any reasonable interpolation of the data from our surfaces.

Several years ago we extracted the temperature dependence<sup>12</sup> of  $\Delta\sigma$  from experiments done on Cs surfaces of various thicknesses<sup>10</sup>. Included in Figure 4 are the results of that analysis for a film with a wetting temperature of 2.179 K, the highest wetting temperature in that earlier sequence of experiments. It seems to conform to the trend of higher wetting temperatures corresponding to stronger temperature dependency of  $\Delta\sigma$ . In Reference 12,

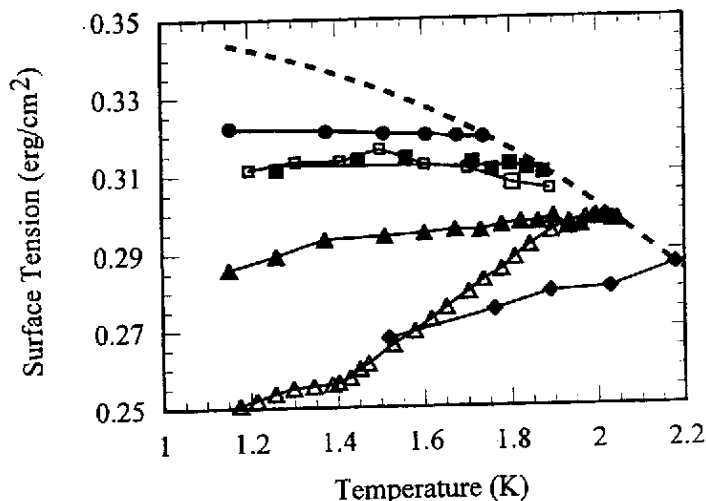


Fig. 4.  $\Delta\sigma$  and  $\sigma_{lv}$  vs. Temperature. The data from surfaces 1-3 are shown as solid triangles, squares and circles, respectively. The diamonds show values of  $\Delta\sigma$  obtained from previous measurements in our laboratory<sup>12</sup>. The dashed line shows  $\sigma_{lv}$  from Ref. 16 on the same scale, and the open triangles show the results for  $\Delta\sigma$  of Ref [8] (referenced to the  $T=0$  value of  $\sigma_{lv}$  from ref 16). The open circles are from Reference 7.

we proposed a model that we used to extrapolate the data shown as solid diamonds in Fig.4 to  $T=0K$ . The present measurements call that model into question as it cannot explain the dependence of  $\Delta\sigma(T)$  on the wetting temperature. The temperature dependence of  $\Delta\sigma$  has important implications for the interpretation of wetting temperature experiments in  $^3\text{He} - ^4\text{He}$  mixtures<sup>11,12,14</sup>. It is clear that the interpretation of those experiments in terms of a  $^3\text{He}$  surface state at the Cs-Helium interface is not a straightforward exercise.

Another difference between the experiments from the various laboratories is the extent of the contact angle hysteresis. In common with Reference 8 our receding contact angles are always close to zero regardless of the surface preparation. Reference 7 reports very small temperature hysteresis. We point out two things. Because of the competing effects of evaporation and thermal expansion, a detailed analysis of the Klier et al.<sup>7</sup> experiment would be required to determine how the temperature hysteresis translates into hys-



teresis in the motion of the contact line. Furthermore it is important to note that contact angle hysteresis is a subtle effect. Counterintuitively, contact angle hysteresis can go to zero in both the large and small roughness limits<sup>17</sup>. One cannot draw simple conclusions about surface quality from the absence of hysteresis.

#### 4. CONCLUSION

We have made direct observations of the contact angle of <sup>4</sup>He on Cs for samples with a range of wetting temperatures between 1.75 K and 2.04 K. Our results show that a single function of T does not describe  $\Delta\sigma$  on all of our Cs surfaces. The temperature dependence of  $\Delta\sigma$  becomes stronger as the wetting temperature increases. Our present results are qualitatively consistent with an indirect determination of  $\Delta\sigma(T)$  we made on a Cs film with a wetting temperature of 2.179 K, but they are not consistent with the model proposed there for the temperature dependence of  $\Delta\sigma$ <sup>12</sup>. Within the combined errors of both experiments, our measurements of the contact angle on a film with a 1.95 K wetting temperature are identical to those of Rolley and Guthmann on a film they studied with the same wetting temperature<sup>8</sup>. In contrast to that experiment, we were able to prepare films with different wetting temperatures by varying the Cs evaporation conditions. Our results disagree with those of Klier et al.<sup>7</sup> The 2.00 K wetting temperature reported by Klier et al. is in the middle of the range of wetting temperatures we studied. Nevertheless, the temperature dependence of  $\Delta\sigma$  they report is nearly twice as strong as the temperature dependence we derived from a film with an even higher wetting temperature. Thus, their result lies outside the systematic trend established by our experiment. Finally, in Reference 12 we used a model to extract the T=0 K contact angle from some even earlier data. The result was 46°. In view of the weakness of the model revealed by this work and the significantly higher wetting temperature of our earlier film, the near agreement with the 48°, T=0 K contact angle reported by Klier et al.<sup>7</sup> should not be interpreted as a support for their result.

It should be noted that our Cs surfaces and Rolley and Guthmann's surfaces were prepared by low temperature evaporation, and Klier et. al. were prepared in an entirely different manner. Thus the contrast between their results and the others may reflect differences in the roughness, crystallographic heterogeneity, or electronic structure of the surfaces. Experiments which analyze the Cs surface independently of its wetting properties seem to us the only way to explore this possibility.

## ACKNOWLEDGMENTS

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