Journal of Low Temperature Physics, Vol. 108, Nos. 1/2, 1997

Rapid Communication

Optical measurement of contact angle of liquid helium on cesium

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(Received December 23, 1996; revised April 4, 1997)

We have studied the wetting properties of helium-4 on a carefully prepared cesium substrate using an interferometric technique. Below the wetting temperature, which is 1.9 K in our experiment, we observe a striking hysteretic behaviour, which is due to the pinning of the contact line on defects of the substrate. We have measured the temperature dependence of the contact angle θ_a for an advancing meniscus. At low temperature, we find $\theta_a \approx 25°$, in contrast with a previous result by Klier et al.[1]

1. INTRODUCTION

The helium-cesium system has been intensively studied during the past few years to investigate the wetting transition.[1-3] We have measured the contact angle of liquid helium on cesium using an interferometric technique. Our main results are these: for temperatures below the wetting transition (which occurs at 1.9 K) there is a well defined, reproducible contact angle for a meniscus which advances into a region where no liquid has been before; in contrast, when a meniscus recedes and then advances into a region it has been before, the contact angle is zero. The system is hysteretic. Only if the cell is emptied by pumping out the helium will one recover the non-zero contact angle.

The great advantage of our optical technique is that we can observe more than just the contact angle and the shape of profile of meniscus: we can also see wetted patches near the contact line and the meandering of the contact line, effects which become more pronounced the closer the system approaches the wetting transition.

0022-2291/97/0700-0001$12.50/0

These observations tell us that the cesium surface is inhomogenous: perhaps there are irregular pits in the surface of the substrate which lead locally to deviations in the contact angle; or perhaps there are local wet patches which could be due to the presence of dust particles leading to local spots which are not plated during the evaporation of cesium; or perhaps there are inhomogeneities which arise during the evaporation of the cesium layer itself. Whatever the mechanism, we believe that there are local patches on the cesium which trap the contact line, and profoundly affect its properties.[4]

The rest of the paper explains these remarks in more detail. First we describe the experimental setup; then we present our results for the contact angle, and discuss the possible origin for the heterogeneity of the substrate; finally, we compare our measurement of the contact angle for an advancing meniscus with the previous one made by Klier et al.[1]

2. EXPERIMENTAL SETUP

We use an helium-4 optical cryostat which can reach 0.8 K. The cryostat is attached to a one ton optical board standing on four air-spring isolators. The light source (He-Ne laser and beam expander) as well as the imaging optics and the CCD camera are outside the cryostat. The bottom of the experimental cell (fig. 1) is made of copper thermally anchored to the 1K pot of the cryostat. On the bottom lies a bare gold mirror of optical flatness $\lambda/20$ (gold and underlying chromium have been evaporated on a silica substrate). The rms mirror roughness is 3 Å.[5] During the measurements, the amount of He is adjusted so that the liquid-gas interface lies between the mirror and the second component of the interferometer, which is a semi-reflecting plate. Its reflection coefficient (~ 0.15) is chosen so that the fringe profile is roughly sinusoidal. The distance between the mirror and the plate is 10 mm, and they are slightly misaligned so that one observes linear wedge fringes in the absence of helium. The field of view is about 15×15 mm. The whole interferometer is tilted by 4° with respect to the horizon so that the triple line (i.e. where the liquid-gas intarface meets the substrate) is straight. Helium can be added or removed at constant rate through the pumping line during the experiment; one can thus move the triple line across the mirror and observe the advancing or receding meniscus.

The preparation of the cesium substrate is made *in situ*, at low temperature, using a commercial getter.[6] The flow rate of these getters has been calibrated previously at 70 K using a quartz microbalance. We have checked that this flow rate is fairly reproducible from one getter to the next, provided that getters are first cycled with a higher current than the one used during evaporation. In the cell, the getter is overheated for 10 minutes; then, the

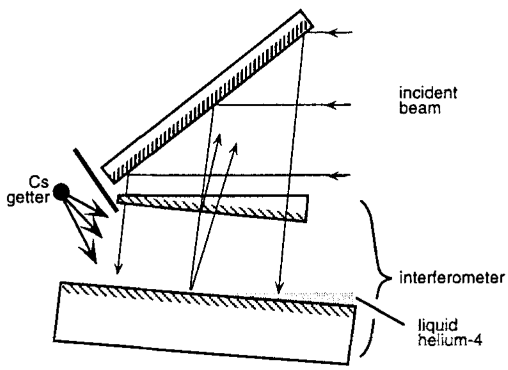

Fig. 1. Schematic drawing of the experimetal setup. The diameter of the mirror is 30 mm and the spacing between the mirror and the semi-reflecting plate is 10 mm.

shutter is opened by a micromotor and Cs is deposited onto the mirror at a rate of around 2 atomic layers per minute. Afterwards the cell is quickly cooled down to 4.2 K. Data reported here have been obtained for evaporation done at 70 and 15 K, and for two different film thicknesses (40 and 120 atomic layers); however, no significant change in the results has been observed.

During the experiment, the helium level is increased at constant rate thanks to a regulated flowmeter. We have seen no dependence of the contact angle on the speed of the triple line, which is usually of the order of 1mm/min. The temperature is measured with a calibrated Ge thermometer[7] attached to the copper base of the cell, next to the mirror. The temperature is regulated during the condensation. During the motion of the triple line, we recorded several images for each temperature over the range 0.8 - 2 K. We have also checked that the contact angle is not dependent on the position of the triple line on the mirror, which shows that the Cs evaporation is homogeneous over the mirror.

The two-beam interferometer provides well contrasted images, and we are allowed to use an ordinary CCD camera with an illumination level of the order of 10 μW/cm^2 at $\lambda = 633$ nm. This heat flux is of the same order as the residual 300 K black body radiation, which is filtered by two pyrex windows located on the 4 K and 77 K shields. We have checked that the shape of the meniscus is not modified when the illumination is ten times larger, which ensures that the effect of the heat radiation is negligible. The fringe pattern in the absence of helium provides a convenient calibration of the magnification which is of the order of $\times 4$ on the CCD.

3. RESULTS

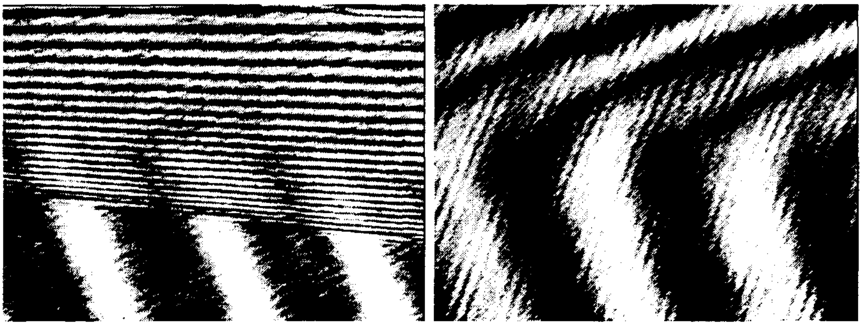

Fig. 2. Interferometric images of an advancing meniscus (left) below the wetting temperature ($T = 0.83$ K) and (right) above the wetting temperature ($T = 1.95$ K). The part of of the mirror covered by the liquid wedge is the upper part of the images. The actual size of the images is 1.85×1.39 mm.

The image shown on figure 2 (left) illustrates a non wetting situation ($T = 0.83$ K); the bare Cs substrate is at the lower part, and the upper part shows cesium covered with He. The corresponding fringe patterns join abruptly (there is a cusp), which implies a finite contact angle. In contrast, the two patterns join smoothly on figure 2 (right); the contact angle is zero at $T = 1.95$ K. Both images correspond to an advancing meniscus on a substrate which has not been previously covered by liquid helium. For an advancing meniscus, the triple line is straight (at least within our optical resolution of 20 μm). The profile is invariant along the line and the contact angle θ_a is well defined. When one gets close to the wetting temperature, typically above 1.6 K, wetted patches can be observed in front of the line, for instance on dust particles. Such patches cause the advancing line to meander with an amplitude which increases as T_W is approached. The measured value of θ_a is thus an average value along the line.

We use two different ways to obtain the contact angle θ_a from the interference patterns, which are equal thickness fringes. When θ_a is larger than about 10°, the measurement of the fringe positions allows us to construct the whole profile of the meniscus. Indeed, a shift of one interference order corresponds to an increase of $\lambda/(2(n-1))$ in the helium thickness, where n is the He optical index.[8] At 2 K, $n - 1 = 0.0286$, so one fringe shift correspond to an helium thickness of 11.1 μm. An experimental profile is shown on figure 3, as well as the profile calculated from the Laplace equation. The good agreement shows that the interface is in equilibrium and that the amplitude of any residual oscillations of the liquid-gas interface is small.

One thus determines the contact angle with an accuracy of 0.5°. For small contact angle, the value of θ_a is rather obtained from the angle between the two fringe patterns, with a poorer accuracy.

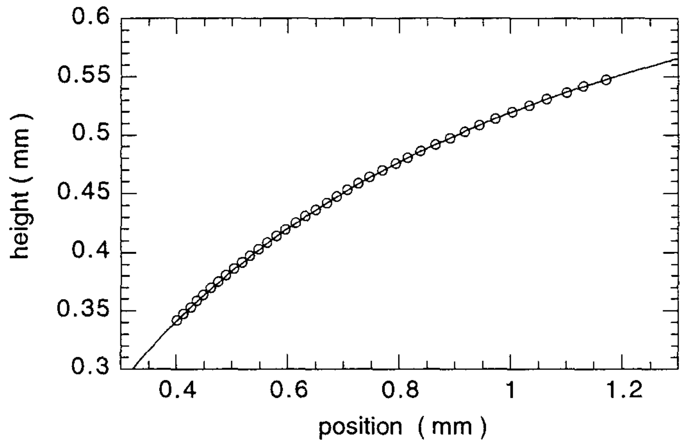

Fig. 3. Experimental profile of an advancing meniscus (dots) at 0.83 K, and theoretical profile (full line). The only adjustable parameter is the position of the contact line. The contact angle θ_a is found equal to 25.5 ± 0.5 °.

At our lowest temperature (0.83 K) θ_a is equal to 25.5±0.5 °. We find that θ_a vanishes at the wetting temperature $T_W = 1.9 \pm 0.05$ K, close to previous determinations of $T_W \approx 2$ K.[1,2] The temperature variation of θ_a is displayed on figure 4.

The wetting properties of the substrate are quite different when it has been previously covered with liquid, which is the case for instance when the meniscus recedes. In this case we always observe a zero contact angle and apparent wetting, as if Cs had been contaminated by helium. The only way to recover a non wetted substrate is to empty the cell. Provided that the cell has been pumped before increasing the liquid level, one finds always the same value of θ_a for a given temperature.

A possible explanation for this huge hysteresis is that some liquid remains trapped in some defects on the substrate, defects which are too small to be observed with our optical set up. These defects could be due to surface roughness or chemical contamination. Indeed, we have measured the optical reflectivity of the mirror during evaporation; the reflectivity is found to be 10 % smaller than the theoretical value computed from the value of complex index of Cs.[9] Since the contact angle is not very big, such a large hysteresis as we see does not require very strong defects. For instance, craters whose borders have a slope of a few ten degrees are able to trap liquid droplets on

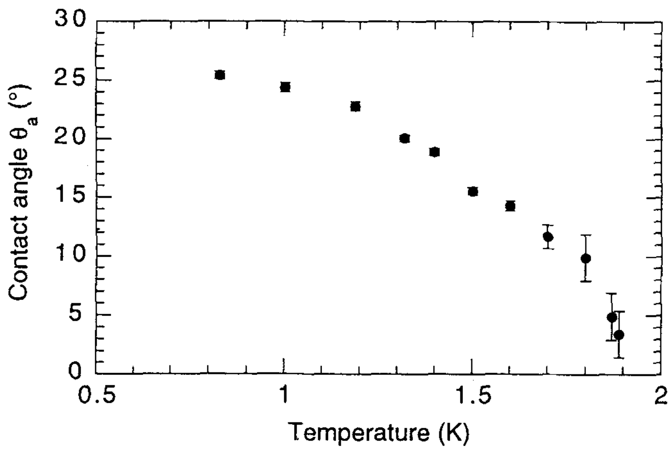

Fig. 4. Plot of the contact angle θ_a for an advancing mensicus as a function of the temperature. The wetting temperature is 1.9 K.

the substrate; local variations of the substrate-liquid surface tension of the order of 10 % are also sufficient to trap the triple line and make dewetting impossible.

We have already performed a few tests to determine the origin of the substrate heterogeneity. First we tried to anneal the Cs layer. The base of the mirror is weakly thermally anchored to the bottom of the cell, so that it can be heated up to room temperature while keeping the wall of the cell below nitrogen temperature. We have not seen any change in the contact angle and hysteresis even when a Cs film evaporated at 70 K is annealed up to 200 K. When annealing at higher temperature, we have observed a drop in the reflectivity, which is presumably due to partial oxidation of the Cs layer. However, the substrate is still not wetted at low temperature, though the contact angles become smaller. As evaporation at 15 K instead of 70 K does not change hysteresis and contact angle, oxydation by residual oxygen in the cell can be excluded, any possible contamination could only be due to the outgassing of the getter itself. As the roughness of the evaporated layer is presumably dependent on the layer thickness, we have performed the same experiment for two different layer thicknesses, namely 40 an 120 atomic layers. No difference was observed, which is an indication that roughness, if present, is not due to the evaporation process itself. As a conclusion, it seems to us that the most probable origin for hysteresis is either a chemical contamination from the getter, or pre-existing micron size defects of the gold mirror itself.

The measurement of the contact angle $\theta(T)$ in equilibrium can yield the temperature dependence of the solid-liquid surface tension σ_{SL}. Indeed, σ_{SL} iS related to θ through Young's relation : $\sigma_{SV} - \sigma_{SL} = \sigma_{LV}\cos(\theta)$, where σ_{SV} is the solid-vapour surface tension. Below the wetting temperature T_W, the coverage of the substrate is expected to be less than one monolayer, and σ_{SV} should have a very weak temperature dependence. As a consequence, the temperature dependence of σ_{SL} is roughly the same as that of $-\sigma_{LV}\cos(\theta(T))$.

The temperature dependence of σ_{SL} is an important parameter which is needed in order to compare experimental data on the phase diagram with theoretical models.[2,3] However, the present situation is rather controversial. Pricaupenko and Treiner[10] have predicted a quasi-linear spectrum for the excitations of the solid-liquid interface, and accordingly a temperature dependence term in σ_{SL} of the order of $7 \times 10^{-4}\,T^3$ K/Å^2. In contrast, there is experimental evidence that the temperature dependence of σ_{SL} is much larger. First, Ross. et al.[11] have performed an analysis of earlier experimental data which yields a decrease of σ_{SL} between 0 and 2 K which is approximately half the decrease of the liquid-vapor surface tension σ_{LV}. A capillary rise experiment performed by Klier et al.[1] has yielded an even larger temperature dependence of σ_{SL} which is roughly the same as σ_{LV}. This is rather surprising, since it implies the existence of some kind of ripplons at the liquid-solid interface.[12]

The heterogeneity of a substrate (due to roughness for instance) is known to promote wetting, and leads to an effective value of $\Delta\sigma = \sigma_{SV} - \sigma_{SL}$ higher than for an ideal substrate. However, our value of T_W shows that the mean value of $\Delta\sigma$ is only slightly higher than the one of other substrates, at least at the transition. So we think it is worth comparing our data with previous measurements, even though the fluctuations of $\Delta\sigma$ could make θ_a significantly different from the value of the contact angle for a perfect substrate.

Our results are displayed on figure 5, where $\sigma_{LV}\cos(\theta_a)$ is plotted as a function of T, as well as the values of $\sigma_{LV}(T)$, taken from Eckart et al.[13] who agree with a more recent measurement by of Roche et al.[14] We find a very weak temperature dependence of $\sigma_{LV}\cos(\theta_a)$, which is fairly reproducible for different cesium substrates. In our opinion, the small differences between the various runs is not due to the temperature at which cesium evaporation was made. Indeed, we paid more attention to avoid dust in the run corresponding to the 4 K evaporation; we think this is the reason why the small bump of $\sigma_{LV}\cos(\theta_a)$ is not observed in this case.

Assuming that θ_a is not very different from θ, and hence that $\sigma_{LV}\cos(\theta_a)$ is close to $\Delta\sigma$, our measurements are consistent with Treiner's prediction. However, our results strongly disagree with those of Klier et al., who find

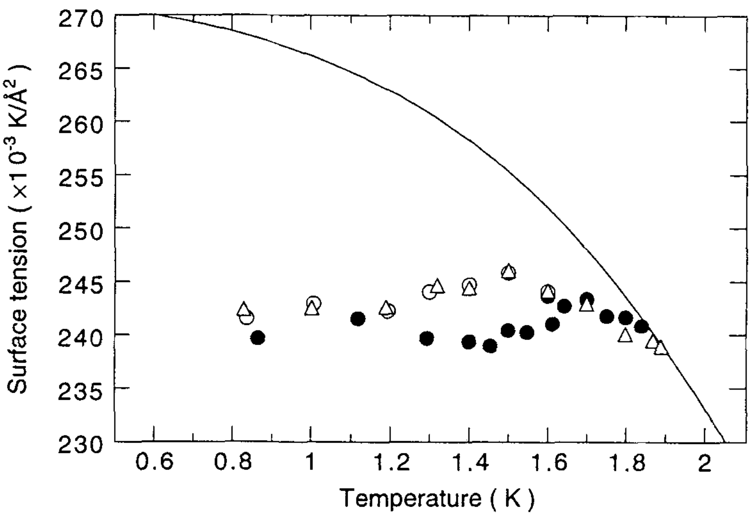

Fig. 5. Plot of $\sigma_{LV}\cos(\theta_a)$ as a function of the temperature. D ifferents symbols correspond to different runs : open circles, just after Cs evaporation at 70 K; triangles, same substrate after annealing at 150 K; full circles, after Cs evaporation at 15 K. $\sigma_{LV}(T)$ [13] (full line) is also plotted. The wetting temperature is 1.9 K, and $\sigma_{LV}\cos(\theta_a)$ is almost independent of the temperature.

$\theta = 48°$ at low temperature, with a small hysteresis. It should be noted that their Cs coating is made by a different method from ours: Cs vapor is condensed on tugsten foils above room temperature. Even allowing for this difference in technique, we have been unable to think of a way of explaining the discrepancy between the two sets of measurements.

4. CONCLUSION

We have observed a strong hysteresis in the contact angle of liquid He on a Cs substrate, even for Cs evaporations which look like perfect mirrors. It seems to us that further precise studies of this system require a better control of the quality of the cesium layer. For instance, without a clear characterization of the substrate, it seems difficult to interpret the observation that the transition from thick to thin film is never observed;[2] this behaviour could be due to the inhomogeneities of the substrate as well as to the thin film nucleation barrier. Other optical techniques could provide some information on the substrate, such as surface plasmons.[15]

On the other hand, the temperature variation of σ_{SL} remains an open question. Our measurement of the advancing angle as a function of the temperature seems difficult to reconcile with those of Klier et al., so that there is still some possibility that the prediction of Pricaupenko and Treiner be valid.

ACKNOWLEDGMENTS

We thank R. Gombrowicz and V. Repain for help in the experiment; S. Balibar, J. Dupont-Roc and J. Treiner for useful discussions; R. Bowley for critical reading of the manuscript. This work was partly supported by CEE grant # CHRX CT 93.0107.

REFERENCES

1. J. Klier, P. Stefanyi and A. F. G. Wyatt, *Phys. Rev Lett.* **75**, 3709 (1995).
2. J. E. Rutledge and P. Taborek, *Phys. Rev. Lett.* **69**, 937 (1992); P. Taborek and J. E. Rutledge, *Phys. Rev. Lett.* **71**, 263 (1993).
3. J. Dupont-Roc and B. Demolder, *J. of Low Temp. Phys.* **101**, 205 (19950.
4. L. Leger and J. F. Joanny, *Rep. Prog. Physics* **55**, 43 1 (1992).
5. Purchased from Melles Griot, Parc du Merantais, 1 rue Guynemer 78114 Magny-les-hameaux, France.
6. SAES Getter / France, 14 rue Drouot 75009 Paris, France.
7. Lake Shore Cryotronics, model GR-200A-250CD.
8. M.H. Edwards, *Can J. Phys.* **36**, 884 (1958).
9. J. Monin, *Acta Electronica* **16**, 139 (1973).
10. L. Pricaupenko and J. Treiner, *J. of Low Temp. Phys.* **96**, 19 (1994).
11. D. Ross, P. Taborek and J.E. Rutledge, *Phys. Rev. Lett.* **74**, 4483 (1995).
12. J. Klier and A. F. G. Wyatt, Proc. of LT XXI, *Czesch. J. Phys.* **46**, 439 (1996).
13. J. R. Eckart, D. O. Edwards and S. Y. Shen, *Phys. Rev.* **B16**, 1944 (1977).
14. P. Roche, G. Deville, N. J. Appleyard and F. I. B. Williams, *J. of Low Temp. Phys.* **106**, 565 (1997).
15. D. Reinelt, H. Gau, S. Herminhaus and P. Leiderer, Proc. of L T XXI, *Czesch. J. Phys.* **46**, 431 (1996).