Experimental Evidence for Nonwetting with Superfluid Helium

P. J. Nacher and J. Dupont-Roc

Laboratoire de Spectroscopie Hertzienne, Département de Physique de l'Ecole Normale Superieure,
24 rue Lhomond, 75231 Paris CEDEX 05, France

(Received 25 June 1991)

Wetting properties of alkali-metallic surfaces by superfluid-helium film have been tested through heat transport. Appearing as an exception among other substrates, cesium is found to interrupt superfluid-film flow, suggesting nonwetting of cesium by superfluid helium. In addition, superfluid-helium films were observed to be only marginally stable on glass having been in contact with cesium vapor.

PACS numbers: 67.70.+n, 67.40.Rp, 68.45.Gd

It is a daily experience for low-temperature physicists that, in an isothermal enclosure containing superfluid helium, a film will cover all available surfaces. This is a manifestation of the fact that liquid helium wets most materials [1]. As opposed to other wetting liquids such as oil, superfluid films have the advantage of reaching thermodynamical equilibrium in a particularly short time. In addition, liquid helium is an extensively studied fluid for which accurate theoretical models exist. In that context, the theoretical prediction by Cheng, Cole, Saam, and Treiner [2] that alkali-metal surfaces may be an exception to this so far universal wetting behavior is particularly interesting. This prediction may be related to a well-established experimental evidence in atomic and molecular physics. Two-body interaction potentials between alkali and helium atoms exhibit extremely shallow wells [3], due to the negative electronic affinity of He and the large size of the alkali outer electron orbital.

We present here the results of an experimental test of the wetting properties of superfluid ^{4}He on sodium, potassium, rubidium, and cesium surfaces. During these experiments, it was also found that a glass surface, presumably modified by the presence of cesium, exhibits peculiar properties with respect to helium films.

When a helium film is in equilibrium with bulk liquid, the film thickness a few centimeters above the bulk surface is on the order of $d_0 = 15$ nm [4], and consequently hardly visible. Nevertheless, the existence of the film is manifested by a very efficient heat and mass transport when one tries to create a temperature gradient. For instance, a 1-cm-wide saturated film can sustain a power flow on the order of a fraction of a milliwatt without appreciable temperature gradient. These heat transport properties rely directly on the existence of a wetting superfluid film, and are hence of interest to test the wetting of a substrate by superfluid helium.

The experimental arrangement is schematically represented in Fig. 1. The sample is a sealed glass tube (inner diameter: $D = 0.4$ cm, length: $l = 20$ cm, wall thickness: $e = 0.1$ cm). The tube was carefully evacuated and degassed, and a small amount of the alkali metal to be tested was introduced under vacuum. Next, the tube was held at liquid-nitrogen temperature, filled with ^{4}He gas (1 ppm grade) under a pressure on the order of 1 bar, and then sealed. Through melting and flowing, a ring of alkali metal was made on the inner surface of the tube, typically a few millimeters wide and a few tenths of a millimeter thick. This ring [5] separates the inner surface of the tube into two topologically disconnected regions. When the sample is cooled down below the condensation temperature T_0 (T_0 is typically between 1.7 and 1.8 K), a volume of a few mm^3 of superfluid liquid is formed in the bottom and a film covers the available inner surface. If the alkali ring is not wetted by the liquid helium, it will interrupt the superfluid film, suppressing this otherwise dominant contribution to heat transport between the two ends of the sample. A tube without any alkali metal was also prepared for comparison.

The heat transport through the sample is measured in the following way. The tube is isolated from the cryogenic bath by vacuum, but its lower end is thermalized to the bath through a copper clamp. An electric heater is attached to the top of the tube. While heating is applied at this point with a power $\dot{Q}$, temperatures are measured at the top, the middle, and the bottom of the tube by carbon-resistor thermometers [6] thermalized to the tube

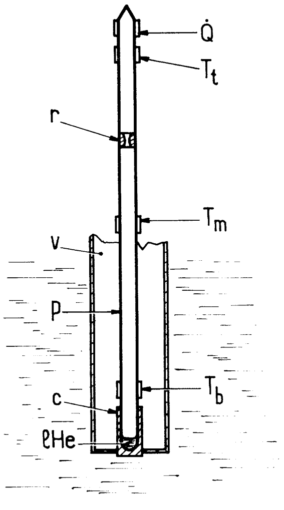

FIG. 1. Sketch of the experimental arrangement. p: Pyrex tube; r: alkali ring; v: vacuum; c: copper clamp; $\dot{Q}$: heater power; T_t, T_m, T_b: measured temperatures.

by copper wires. These temperatures are denoted, respectively, T_t, T_m, and T_b.

It is well known [4] that under a thermal constraint, a superfluid film will remain practically isothermal by a displacement of the superfluid component towards the heat source. In our experiment, heat transport takes place through evaporation of the film at the heat source and recondensation at the heat sink, the sample exhibiting a nearly zero thermal resistance $(T_t - T_b)/\dot{Q}$ [7]. This situation is maintained as long as the film can sustain the superfluid flow. If the critical velocity is exceeded, or if the film is evaporated ("burnt"), there will only remain a much weaker heat conduction by the glass and the gas, resulting in a large temperature gradient across the sample.

This is indeed what is observed, with the difference that, in general, two different burning thresholds are found. The upper part of the superfluid film disappears, as revealed by a change in $T_t - T_b$. The lower part of the film (which lies entirely on glass) is burnt only at a higher power, with this second threshold being detected on $T_m - T_b$. The powers corresponding to the burning thresholds are given in Table I. Most of them are in the range 0.1–0.2 mW. A noticeably different value is obtained for the upper film in the sample containing the cesium ring which is burnt by a power as low as 0.006 mW. This peculiarity was reproduced with two different samples, and several times on a given sample, the cesium ring having been melted and reshaped.

We determined the thermal resistance $(T_t - T_b)/\dot{Q}$ for each sample below the first threshold. In this situation, the superfluid film is supposed to cover the glass surfaces and possibly the metal ring, if it is wetted. Except for cesium, the thermal resistance was found to be zero, with an experimental error ± 0.1 mK/μW. For cesium, the thermal resistance was finite. Its value was on the order of 2 or 3 mK/μW, depending on the sample. This resistive behavior is shown in Fig. 2. We observed in addition that T_m and T_b remain equal, indicating that the thermal impedance lies in the part of the tube containing the cesium ring. The magnitude of this finite thermal resistance is the crucial experimental observation. It is not compatible with the existence of a continuous saturated film inside the sample, with critical flows similar to usual ones.

The most probable explanation is that cesium is not wetted by liquid helium and interrupts the superfluid film. Two superfluid films exist in the sample, the upper one in close contact with the heat source, the lower one thermalized to the bath, separated by the cesium ring. It is to be emphasized that this situation is quite uncommon, since a superfluid film in thermal equilibrium normally has no border [8].

TABLE I. Heating powers in mW for film burning. Error is typically ± 2 on the last significant figure.

	Alkali metal				
	None	Na	K	Rb	Cs
Upper film	0.22	0.12	0.08	0.13	0.006
Lower film	0.22	0.15	0.17	0.21	0.24

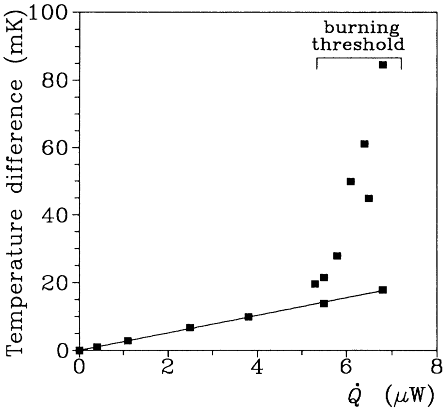

FIG. 2. Temperature difference across the cesium ring vs heater power, showing the finite thermal resistance. The straight line is fitted on the low power points. Near the burning threshold, a hysteretic behavior is observed.

The value of the thermal resistance may be accounted for as follows. The two films are thermally connected through the helium vapor, the glass substrate, and the metal ring itself. Orders of magnitude for the corresponding thermal resistances are, respectively, 50, 10, and 0.03 mK/μW, to which Kapitza resistance has to be added (the alkali-metal thermal conductivity is assumed to be 1 W/cm K [9]). Because of the nonwetting, the contact between the cesium metal and the helium film reduces to a very small area whose transverse dimension is likely to be on the order of the film thickness d. The corresponding Kapitza resistance is evaluated to be about 10^3 mK/μW and prevents direct heat flow between the films and the metal. In fact, heat has to flow around the contact lines via glass or gas. A simple model, assuming that both the helium film and the metal are quasi isothermal, shows that heat has to travel in glass over a distance on the order of the glass thickness e, and yields a thermal resistance of 1 mK/μW for each contact, in reasonable agreement with the experimental values. The gas contribution is estimated to be an order of magnitude smaller.

Hence it appears that, in our experimental conditions, cesium interrupts superfluid helium films, but that a superfluid film covers the other alkali metals studied. The foregoing conclusions are in agreement with the theoretical predictions of Cheng *et al.* [2] concerning Cs, but not for K and Rb for which nonwetting is predicted. It should be noticed, however, that pure, flat alkali surfaces are assumed for the theory. How well are these hypotheses realized in our sample?

Although the tube was pumped and degassed above 100 °C for several hours prior to the introduction of alkali metals, it is still likely that outgassing from the glass wall introduces oxygen and water in a sufficient quantity to cover the alkali surface. Even if the high density of helium may efficiently slow down their diffusion through the sample, they will eventually reach the alkali and react with it. Fortunately, it is known that, for cesium and rubidium at least, the oxides are dissolved in the bulk of the metal [10], and so the surface may keep a metallic character. Between successive experimental runs, the metals have also been melted and reshaped in order to renew their surfaces, but no significant alteration of their visual aspect was observed even weeks after the preparation of the sample. We feel that the metallic surfaces tested were as clean as possible in a practical sense, but presumably contain a certain amount of oxides. Note, however, that surface oxides should favor wetting, by providing stronger binding sites for He atoms than the metallic surface itself.

Another parameter to be discussed is the microscopic shape of the surface. It is known [11] that rough surfaces have wetting properties which can be different from those of flat ones. For instance, wetting and drying contact angles can be different. In helium-film physics, it has been noticed that "dirty" surfaces tend to be wetted by thicker films than are clean ones [4]. Also, an etched silicon surface has been shown to adsorb an excess volume of film in a certain thickness range [12], which is equivalent macroscopically to a stronger wetting. It is thus possible that a rough surface made with an otherwise nonwettable material could nevertheless be wetted by a helium film. To summarize, the discrepancy between the theoretical predictions and the experimental results should not be necessarily attributed to imperfections of the theory, or to the inaccuracy of the substrate-helium potentials used. Surface oxides, surface roughness, or contamination should favor wetting. In that context, the nonwetting on cesium appears most remarkable.

Now the burning thresholds remain to be explained. The values of Table I in the range 0.1–0.2 mW are consistent with a maximum film flow on the order of 5×10^{-5} $\mathrm{cm^2\,s^{-1}}$, which is a typical value for a saturated film [4]. Reduction from this standard value may be brought by the diminution of the film perimeter on the ring. Except for the case of cesium, the film burning occurs between 1.6 and 1.8 K. For Cs, burning in the upper part was observed for temperatures as low as 1.33 K, well below $T_0 \simeq 1.8$ K. The observed burning power for cesium was not affected significantly by the temperature which has been varied from 1.3 to 1.65 K. A hysteretic behavior is observed as the power is increased or decreased as shown in Fig. 2. This hysteretic behavior suggests the existence of a nucleation barrier to reinstall a superfluid film in the upper part after burning.

In order to investigate the burning mechanism of the upper film, a second electric heater was attached on the sample, just at the level of the cesium ring. Because of the thermal resistance between the cesium and the lower film, it was possible to vary significantly the temperature difference between the two films by applying a power $\dot{Q}'$ of a few microwatts using this second heater. It allows us to vary independently the heat flow in the upper film and the temperature difference between the upper and the lower film. In Fig. 3 the temperature difference across the cesium ring at the burning threshold of the upper film is shown for various heat fluxes in this film. It appears clearly that the burning of the upper film is not related to some critical heat flow in it, but rather to a temperature difference between this film and the rest of the sample. This difference, namely, 10 ± 2 mK is surprisingly small, indicating that the upper superfluid film is near a stability limit. The corresponding difference $\mu_t - \mu_b$ in the chemical potential may be calculated easily, assuming that each film is in thermal equilibrium with the vapor facing it. The pressure being through the sample (neglecting the weight of the vapor column), the variation of the chemical potential in the vapor reduces to

$$\mu_t - \mu_b \simeq -s_v(T_t - T_b) \simeq -(s_l + L/T_b)(T_t - T_b)\,, \qquad (1)$$

with s_v and s_l being the liquid and vapor molar entropies, and L being the latent heat of vaporization. The numerical value of $\mu_t - \mu_b$ is found to be typically 70 mK. It corresponds to a relative variation of the saturation pressure of at most 5%, far below what is known to correspond to the suppression of superfluidity in helium films on glass (typically 50%) [13]. Hence this suggests that the glass surface may have been modified. Indeed, the vapor pressure of cesium at room temperature is sufficient

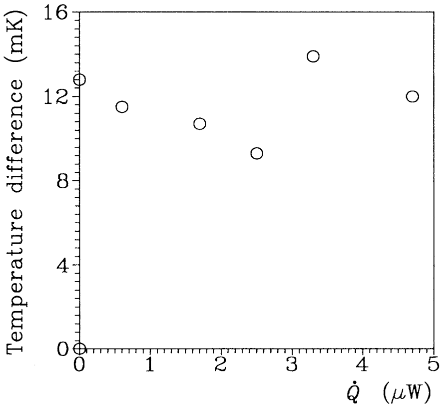

FIG. 3. Temperature difference across the cesium ring at threshold, vs the heat flux $\dot{Q}$. For a given value of $\dot{Q}$, the temperature difference is adjusted using a second heater located at the level of the Cs ring. The point at the origin corresponds to no heating at all [6]. This shows that the burning of the upper films is correlated with the temperature difference rather than with $\dot{Q}$.

to form a monolayer in less than 1 s and it is likely that, during the sample preparation, the glass surface has been covered with cesium atoms. Because of the large core radius of the He-Cs potential (~0.5 nm), even a submonolayer would drastically weaken the wall attraction at short distance, causing the surface to be only marginally wetted by liquid helium. Hence, a small difference between the chemical potentials in the two parts of the tube would be sufficient to dry the upper one. In an attempt to get more information on the transition mechanism, two thermometers were installed on the upper part of the tube above the cesium ring. The temperature of the upper film was brought to its burning temperature. The temperature of the upper thermometer rose first, followed a few minutes later by the second one. This indicates that the disappearance of the upper film occurs by the displacement of a front from the top of the tube to the cesium ring. A direct measurement of the film thickness would be of much interest to elucidate the exact nature of this burning process, because it may represent an interesting example of a prewetting transition [14].

We thank the authors of Ref. [2] for the communication of their results prior to publication, and S. Balibar, G. Tastevin, and G. Vermeulen for the kind loan of equipment. We are indebted to G. Flory for his help in preparing the samples. We are grateful to N. Bigelow for helpful comments about this manuscript. Laboratoire de Spectroscopie Hertzienne is a Formation de Recherche de l'Ecole Normale Supérieure et de l'Université Pierre et Marie Curie, associée au Centre National de la Recherche Scientifique.

---

[1] However, finite thickness at saturation instead of diverging growth has been claimed. See A. D. Migone, J. Krim, J. G. Dash, and J. Suzanne, Phys. Rev. B **31**, 7643 (1985); P. Taborek and L. Senator, Phys. Rev. Lett. **57**, 218 (1986).

[2] E. Cheng, M. W. Cole, W. F. Saam, and J. Treiner, Phys. Rev. Lett. **67**, 1007 (1991).

[3] J. Pascale, Phys. Rev. A **28**, 632 (1983).

[4] J. Wilks, *Liquid and Solid Helium* (Clarendon, Oxford, 1967), Sec. 14.

[5] Alkali metals were found to stick quite well to glass. It was checked that a plug of sodium metal inside the tube is leak tight even against superfluid helium.

[6] Calibration of the thermometers was made separately in a pumped ^{4}He bath. The temperature was deduced from vapor pressure measurements. The overall errors on temperature differences are currently about 20 mK. For some particular experiments, the resolution was increased by a factor of 10. Because of thermal cycling, the temperature scales of the various thermometers shifted a little from one experiment to another. Temperature differences were taken as zero when no power was injected in the sample.

[7] A lower limit is introduced by the flow impedance experienced by the vapor return flow and the temperature gaps between the vapor and the film necessary for the evaporation and recondensation processes at both ends. In the present situation, this minimum can be evaluated to be negligible.

[8] Note that a border is predicted if very large heights above the bulk level are considered. See J. F. Joanny and P. G. de Gennes, C. R. Acad. Sci. **299**, 605 (1984).

[9] This value is taken from Table 4*g*-8 in the *AIP Handbook* (McGraw-Hill, New York, 1972), where it is given for a pure metal at 4.2 K. We do not expect our sample to be entirely oxide free, so that its thermal conductivity is possibly lower than that.

[10] J. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans, Green and Co., London, 1927); P. Pascal, *Nouveau traité de Chimie Minérale* (Masson, Paris, 1957), Vols. II and III.

[11] See, for instance, M. O. Robins, D. Andelman, and J. F. Joanny, Phys. Rev. A **43**, 4344 (1991), and references therein.

[12] D. T. Smith and R. B. Hallock, Phys. Rev. B **34**, 226 (1986).

[13] G. B. Hess and R. J. Muirhead, J. Low Temp. Phys. **49**, 481 (1982).

[14] C. Ebner and W. F. Saam, Phys. Rev. Lett. **38**, 1486 (1977).