Surface Tension of Solid ^{4}He

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The interfacial surface tension and the angle of contact between superfluid ^{4}He and bcc and hcp ^{4}He crystals have been measured in the same way as for a free liquid surface. Contrary to expectations, neither crystal is found to "wet" the wall of the container. At 0.4 K the surface tension between hcp ^{4}He and the liquid is 2.5 times larger than that between liquid and vapor.

We report the first direct measurements of α_{ls}, the surface tension, or surface free energy, between solid and liquid helium, and of the angle of contact θ that the solid-liquid interface makes with the wall of the container. The angle of contact is related[1] to the difference in surface free energy between liquid helium in contact with the wall α_{lw}, and solid helium and the wall α_{sw}:

$$\alpha_{ls}\cos\theta = \alpha_{lw} - \alpha_{sw}. \tag{1}$$

This relation is an equality, rather than an inequality, since experimentally $|\cos\theta| < 1$.

The measurements have been made between 0.4 and 1.7 K for both the hexagonal (hcp) and the body-centered cubic (bcc) phases of ^{4}He. The results are interesting for a number of reasons. First, they show that it is possible to measure the surface tension in the same way as for a free liquid surface. Secondly, α_{ls} can be compared to estimates inferred[2,3] from the mobility of positive ions in the liquid, using the Atkins[4] "snowball" model. At 1.7 K the agreement is surprisingly good in view of the small diameter of the ion (16 Å). However, the direct measurements indicate that α_{ls} has a considerable temperature dependence, and that it increases very substantially below 1 K. Thirdly, our measurements of θ show that neither hcp nor bcc ^{4}He "wets" the copper surfaces used in the experiment. This contradicts the theory of Landau and Saam[5] that the dense, adsorbed film of "surface solid" which is observed[5] on a substrate in contact with the liquid is simply ordinary solid He which is at an increased pressure as a result of the van der Waals attraction of the substrate. If this theory were true, in our experiment the film would become infinitely thick as the liquid approach solidification pressure, so that the solid phase would completely wet the wall and the angle of contact θ would be zero. In fact, $\cos\theta$ is observed to be *negative* ($\theta > 90°$), which implies from (1) that $\alpha_{lw} < \alpha_{sw}$ and that it is energetically favorable to have the liquid near the wall, rather than the solid.

The experimental method is illustrated in the insets to Figs. 1 and 2, each of which shows cylindrical copper capacitor intersecting the interface between the liquid and the ^{4}He crystal. The method is based on the fact that, since the liquid is superfluid, equilibrium with regard to both pressure and temperature is nearly perfect, so that the solid-liquid interface outside the capacitors is quite flat and horizontal. This has been checked experimentally in these and other experiments on the propagation of second sound and of ballistic heat pulses in the same cell.[6] It has also been verified that the solid is a single crystal which may be partially melted and refrozen so as to move the solid-liquid interface up or down as required. In the present experiments, the position of the interface was determined by (a) measuring the amount of ^{4}He added or removed through

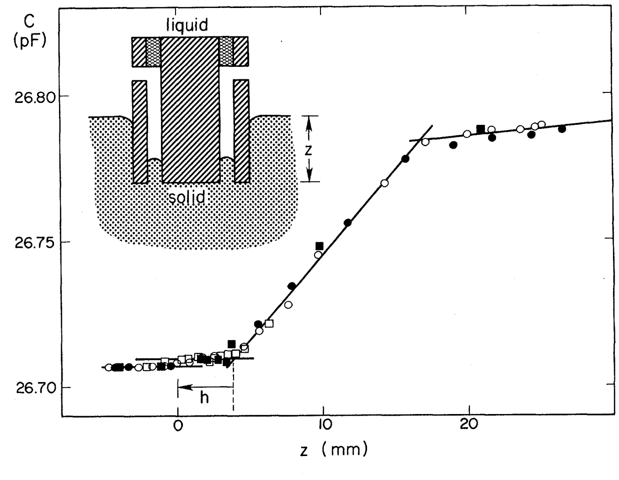

FIG. 1. Measurement of the capillary depression $-h$ at 1.31 K: capacitance C versus z. The inset shows a cylindrical capacitor immersed in the solid to a depth z. The small increase in C at $z=0$ is due to the edge capacitance as the solid reaches the bottom of the capacitor; the solid enters the annular space at $z=-h=3.9$ mm, and the capacitor is full at $z=16.7$ mm. Filled circles, initial decrease of 2; open circles, first subsequent increase of 2; filled and open squares, a second cycle, decreasing and increasing z, respectively.

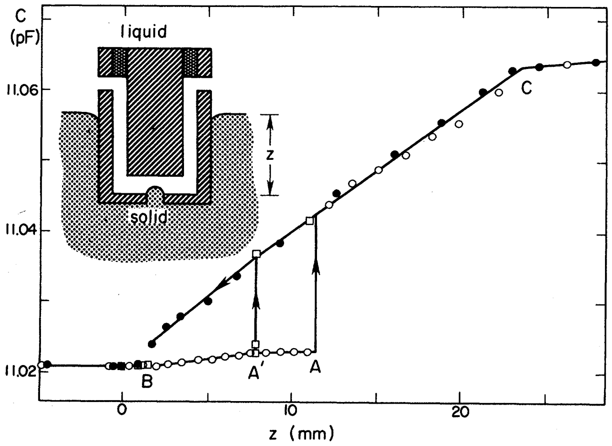

FIG. 2. The "hole" capacitor at 0.4 K: capacitance C versus level z. The hole radius r was 1.0 mm. The inset shows the situation when the solid is about to enter the capacitor. A on the graph. Open circles, initial increase of z; filled circles, first subsequent decrease; squares, second increase. The capacitor empties at B and the small increase in C between $z = 2$ and $z = 7$ mm is due to the leads.

the filling tube, (b) observing when the interface passed above or below a heater and bolometer pair which could be used to propagate ballistic heat pulses or second sound, and (c) monitoring the level with a third cylindrical capacitor with a wide annular gap (1.5 mm). The accuracy of these level measurements was approximately ± 0.2 mm.

The method of measuring α_{ls} and θ can best be understood by initially thinking of the solid as though it were an isotropic fluid rather than a crystal. Thus, the capacitor shown in Fig. 1 measures, in the usual way, the capillary rise h which is related to $\alpha_{ls}\cos\theta$:

$$h\Delta\rho g d = 2\alpha_{ls}\cos\theta.$$

Here $\Delta\rho$ is the difference in density between liquid and solid, which is known very accurately,[7] g is the acceleration due to gravity, and $d = 0.30 \pm 0.01$ mm is the width of the gap between the inner and outer conductors.

Since in fact the level was observed to be *depressed* inside the capacitor, both h and $\cos\theta$ in (2) are negative. Some data are given in Fig. 1 which show that h does not depend on whether the level of the crystal is being raised or lowered. In all the experiments the level was changed in steps at a rate of ~ 1 mm/min. At each step, equilibrium was established within a few minutes or less.

The second capacitor, that shown in Fig. 2, was used to measure α_{ls} by the "bubble" method. The level of the solid was gradually raised until a sudden jump in the capacitance indicated that the solid had entered the bottom of the capacitor through the accurately machined hole of radius r. At the moment of entrance, the meniscus is approximately hemispherical with radius r so that the level difference H is given by[8]

$$H\Delta\rho g r = 2\alpha_{ls}. \tag{3}$$

Note that, just before the solid enters, the liquid inside the bottom of the capacitor is in a metastable state, above the melting pressure. Some data at 0.4 K are shown in Fig. 2. In this experiment, the second time the solid entered the capacitor, at A', it did so at a somewhat smaller level difference ($z = 8$ mm instead of 11 mm). It was found that such events could be triggered by vibrations, pressure, and temperature fluctuations, etc. We therefore calculated α_{ls} from the largest static level difference observed.

Of course, the description of the experiments above is oversimplified in two ways. First, we have treated the solid as though it were a fluid. Although this is not true, some thought shows that the shape and position of the interface in each capacitor does not depend at all on equilibrium being established throughout the solid phase but only in that part of it which is in contact with the liquid. Moreover, equilibrium of the interface can be established through the liquid alone. It is important, therefore, that the capacitors have holes near the top to give access through the liquid.

The second simplification is that we have treated the solid as isotropic. In principle, the surface tension of a classical crystal is a function of the orientation of the surface with respect to the crystal axes and it has local minima at all the principal directions.[1] This means that the equilibrium meniscus may not be cylindrical or spherical, but it may have a number of facets. The angle of contact θ might also be expected to depend on the crystal orientation. The values of α_{ls} and θ from (2) and (3) are therefore averages over certain crystal directions which, since the capacitors have cylindrical symmetry, should depend on the angle between the vertical axis and, for example, the c axis of the hcp crystal. Although the orientation of each crystal is probably random,[6] we have not observed any large variation in α_{ls} or θ from one experiment to another. Another effect of anisotropy is that the height of

TABLE I. Interfacial free energies between liquid ^{4}He, solid ^{4}He (hcp or bcc) and the walls, and the angle of contact θ.

T (K)	$\alpha_{ls}\cos\theta = \alpha_{lw} - \alpha_{sw}$ (erg cm^{-2})	α_{ls} (erg cm^{-2})	θ (deg)
	hcp		
0.40	-0.11 ± 0.03	1.00 ± 0.15[a]	97
0.44	-0.12 ± 0.03	0.87 ± 0.10[b]	98
0.77	-0.11 ± 0.015	0.96 ± 0.10[b]	97
1.29	-0.137 ± 0.01	0.145 ± 0.01[c]	~160
1.31	-0.10 ± 0.01	0.107 ± 0.01[b]	~160
	bcc		
1.67	-0.076 ± 0.01	0.098 ± 0.015[b]	~140

[a] Measured with hole radius r equal to 1.00 mm.
[b] Measured with hole radius r equal to 0.62 mm.
[c] Measured with hole radius r equal to 0.255 mm.

the meniscus in the capacitor of Fig. 1 may not be uniform, but it might vary with the azimuthal angle. The entrance of the solid into the annular space in Fig. 1 would then be rounded rather than well defined. Some rounding has been observed, particularly at 0.4 K, but we are not yet certain that it is due to anisotropy.

The results for α_{ls}, $\alpha_{lw} - \alpha_{sw}$, and θ from the experiments are shown in Table I. The principal conclusions are as follows:

Neither bcc or hcp wets the capacitor walls. This is not just a property of copper since, prompted by the present work, Landau, Lipson, and Maattanen[9] have recently made optical observations of the hcp interface at 0.8 K, obtaining $\theta \sim 120°$ for the glass windows in their apparatus. This agrees fairly well with our value of θ at 0.77 K. They observed the interface to be angular and faceted during rapid growth of the crystal, but rounded with perhaps one or two small facets when in quasiequilibrium with the liquid.

As mentioned earlier, the fact the neither crystal wets the wall disagrees with the theory of Landau and Saam.[5] Nevertheless, Landau and Saam were able to fit their measurements of the adsorption from the liquid onto a Grafoil substrate by assuming the adsorbed film to be ordinary bcc ^{4}He. One possibility is that their data could be fitted equally well by assumption of some other structure which is neither hcp nor bcc. For example, the film might be fcc, stabilized by the effect of surface energy. Since, in our experiments, the adsorbed film failed to grow continuously into either of the bulk solid phases, adsorption from the liquid seems to be type II in the classification recently discussed[10] by Dash and Peierls.

Table I also shows that α_{ls} has a strong temperature dependence, from ~1 erg cm^{-2} at 0.4 K to ~0.1 erg cm^{-2} above 1 K. Since $-d\alpha_{ls}/dT$ is the surface entropy, this implies a highly disordered interface in the region of 1 K. It is interesting also that α_{ls} is not much changed by the transition from hcp to bcc at 1.46 K. Both of these effects may be due to a reconstruction of the hcp surface which is related to the structure of the bcc phase.

Finally, α_{ls} for bcc agrees quite well with the estimates from the positive-ion mobility, 0.04 erg cm^{-2} at 1.8 K to 0.1 erg cm^{-2} at 1.95 K.[2,3] Below, 1 K, where α_{ls} for hcp becomes much larger, the ion radius near melting has not been determined[11] from the mobility. The direct measurements of α_{ls} indicate a factor-of-2 decrease in the radius of the ion in this region, if its structure were hcp.

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