

THE SURFACE OF SOLID HELIUM

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This article is dedicated to the memory of Judah Landau who died on 28 March 1981 after a long illness

This paper describes some of the macroscopic equilibrium properties of the interface between a helium crystal and liquid ^4He or a dilute solution of ^3He in ^4He . The evidence for a roughening transition in the interface at 1.08 K in pure ^4He is described as well as measurements of the anisotropic surface tension. The possibility of surface structure in dilute solid mixtures is raised, based on observation of the way in which crystals melt. Most of the experimental evidence discussed was obtained by the use of holographic interferometry, and related optical techniques.

This paper describes some of the macroscopic properties of the interface between a helium crystal and liquid helium. For the greater part, pure ^4He will be considered, but we shall also hint at interesting discoveries in dilute ^3He – ^4He mixtures.

Most of the recent developments in this field have arisen out of direct observation – as a result of looking at crystals. This is not difficult to do; one needs a cryostat with windows, a light source (usually, today, a weak He–Ne laser) and a camera. Various image-processing methods have also been used: spatial filtering, diffraction, polarization, interferometry and so on. As an example, the optical system used in our work is shown in fig. 1, which is self-explanatory.

First of all, how does helium solidify? As everyone knows, there is no triple point, so the question really relates to the various solid and liquid phases. The phase diagram (fig. 2) shows h.c.p., b.c.c. and f.c.c. solid phases; the former two can coexist either with superfluid or with normal fluid.

Historically speaking, the first experiments which were relevant to today's discussion were

those done by Vos [1] in Delft. He was particularly interested in the h.c.p. phase at high pressures, and used polarization microscopy as his observation tool. He was mainly concerned with the optical anisotropy of this phase. He reached the h.c.p.–f.c.c. transition (above which the crystals are isotropic again) but also made a few observations which are relevant to this article at much lower pressures, in the h.c.p.–

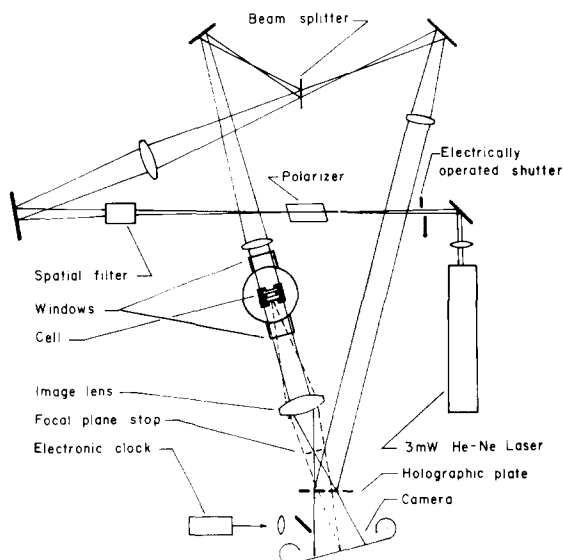


Fig. 1. Optical system used for holographic interferometry.

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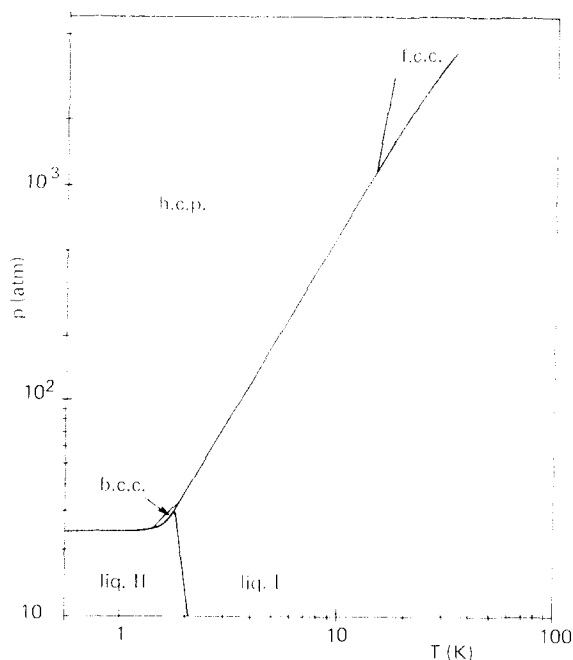


Fig. 2. Phase diagram of pure ^4He .

superfluid coexistence region. In general, Vos showed that solid helium easily forms large single crystals and that at high temperatures the crystal surfaces are not faceted. He also produced a cine-film of his work, and one can see from it that the crystals are faceted while they grow. Further work on solid helium at high pressures has been done recently by Franck [2] who is mainly interested in the h.c.p.-f.c.c. transition.

In recent years, a much more intensive study of the solid surface has started. Helium is, of course, very convenient for surface studies of any sort because of the absence of contamination problems. Our interest in the subject was awakened by Balibar, Edwards and Laroche [3] in Paris, who measured the surface tension of solid ^4He by finding the pressure necessary to force the solid through a hole of about 1 mm diameter. In addition, they measured the capillary rise of the solid in a tube, and found it to be negative. With these two measurements, one can deduce the surface tension, γ , and the angle of contact. Surprisingly the negative capillary rise suggested that solid helium does not wet sur-

faces, and this in spite of the proven existence of a monolayer, at least, of solid helium on all surfaces in contact with the liquid. This phenomenon is still not really understood in microscopic terms. A second observation by these workers was a sudden step in γ at about 1 K, which led to hardly credible thermodynamic consequences. In parallel, speculations by Andreev and Parshin [4] in Moscow based on the observation that helium crystals are rounded in form at very low temperatures, suggested that solid helium shows very specific quantum crystal properties. But it turned out that helium crystals *are* faceted at low temperatures, and the situation is more complicated and interesting.

These observations sparked off our own interest in the subject. Together with my late colleague, Judah Landau, and our graduate students, I was working the diffusion of ^3He in isotropic helium mixtures using an optical cryostat with holographic interferometry as the basic analytical tool. The ^3He acted as a "tracer" because the refractive index of the mixture depends critically on its concentration, and can be mapped by interference techniques. When Edwards told us of the remarkable discoveries [3] in pure ^4He we immediately looked at crystals of the solid grown at low temperatures and confirmed the non-wetting properties. In addition we saw how the crystals grow, faceted, and relax into more-or-less free meniscus form within a very short time of their growth. Such quick equilibration in the solid phase is unknown in any other solid. The meniscus shape allowed us to determine [5] the surface tension γ and contact angle by a completely independent method to that used by Balibar et al. [3] and we found their contact angle to be substantially correct, as was their value of γ above 1 K; but the step in γ was absent; the surface tension was independent of temperature.

To use the meniscus shape in order to calculate γ we found, as a purely empirical measure at first, that it was not possible to use any observed meniscus. Some menisci retained facets, particularly near the horizontal (fig. 3). This

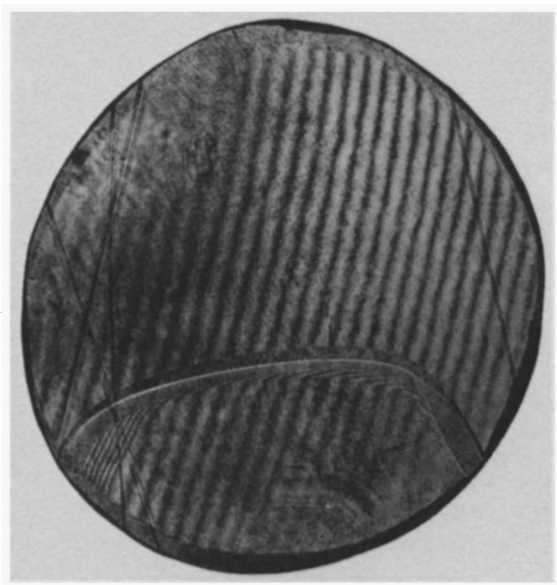


Fig. 3. Holographic interferogram of a solid helium meniscus, showing some facets.

phenomenon occurred mainly at low temperatures; all b.c.c. and “hot” h.c.p. crystals were classically shaped.

About this time J. Avron, who was temporarily in our department, became interested in the mathematical aspects of a possible transition in the surface of a crystal between atomically rough and atomically smooth states. Called a “roughening transition”, this had been predicted by Burton, Cabrera and Frank [6] in 1951, and a single observation in diphenyl [7] was the only evidence of its reality.

Consider a high-symmetry crystal surface containing few dislocations or other defects. On this surface there will generally be numbers of adsorbed atoms; these will diffuse around until they are trapped by a defect, and in this way the crystal grows. We are interested in the statistics of these adsorbed atoms, which contribute to the surface energy because they have fewer satisfied bonds than do atoms lying in the surface. The adsorbed atoms attract one another, thereby reducing the surface energy, and tend to form islands.

If we denote an adsorbed atom by $\mu = 1$, and a position without an adsorbed atom by $\mu = -1$,

we immediately see the analogy between this system and the two-dimensional Ising model. The interaction between neighbours is given by $\frac{1}{2}\phi(1 - \mu_1\mu_2)$, where ϕ is the bond energy, which can be approximated by the surface energy per atom.

The known solution to this problem tells us that there will be a transition from an ordered “atomically smooth” state to an “atomically rough” one in which the adsorbed atoms are in essentially uncorrelated positions. The transition temperature is T_R , where

$$kT_R = \phi K$$

and K is a number of order unity whose value depends on the model used for the calculation.

For the simplest square-lattice model $K = 0.6$; for a triangular lattice (equivalent to the basal plane of the h.c.p. structure), $K = 0.9$. For a rectangular lattice with anisotropic interactions K can take any value between 0 and 0.6. The addition of further layers (μ can take any integer value) makes relatively little difference to the results.

Using measured values for the surface tension [5] we estimate the roughening transition for the (0001) plane to occur at 1.2 K and expect that different crystal orientations should have different transition temperatures. In most other materials the transition would occur above the melting point, according to this criterion!

One should point out at this stage the reason that Andreev and Parshin [4] found the rounded equilibrium form of helium crystals so important. If it were indeed true, the implication of a rough surface at absolute zero would imply completely non-classical behaviour, since the arguments of Burton et al. show that all crystals must become faceted at low enough temperatures, where the TS term in the free energy becomes negligible. However, we must also emphasize that the difference between a partially-faceted and continuously curved surface is in practice quite small, and we should probably not have noticed it had we not made accurate numerical analyses

of the surface profiles in order to measure the surface tension.

In this situation, we tried to pinpoint the transition between the region of rounded meniscus crystals and faceted crystals. Gravity, by flattening out all reasonable sized crystals, made it difficult to sense any abrupt change in shape. The most definite observation [9] was made in a very small crystal (about 1 mm dimension) whose shape was little affected by gravity. Analysis of interferograms of the crystal shape showed a definite reversible change at 1.08 K (fig. 4). Later (before the announcement was finally accepted for publication) we found in the same set of interferograms a second morphological transition between 0.8 and 0.9 K. The ratio between these two temperatures agrees quite well with Avron's prediction for the (0001) and (11 $\bar{2}$ 0) faces, which are the only ones observable in pure solid helium.

The roughening transition provides a natural explanation [9] of the abrupt change in γ in the results of Balibar et al. [3]. Once facets become stable, the geometry of the solid growing through a circular hole becomes quite different, and the results for γ below the transition become invalid. In addition, further evidence for the same transition in helium in the (0001) plane came independently from Keshikev et al. [10] in Moscow, at about the same time, so that the upper transition temperature, at least, appears to be an established fact.

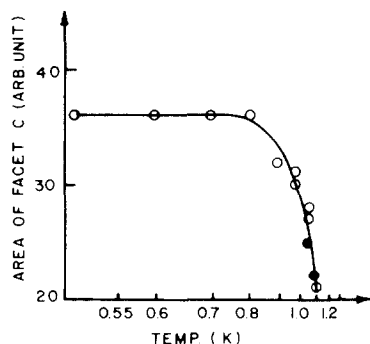


Fig. 4. Area of the (0001) facet of a small ^4He crystal, going through the roughening transition: \circ increasing temperature, \bullet decreasing temperature.

It is interesting to look at the shape of the transition in terms of the anisotropy of γ . In any material the shape of the equilibrium crystal is determined once the variation of γ with surface orientation is known. The result is described geometrically by Wulff's construction and its implications with various degrees of anisotropy are discussed thoroughly by Herring [11]. What is rather interesting is that only the sums $\gamma + \gamma_1^{(1)}$, and $\gamma + \gamma_2^{(1)}$ are important in determining crystal shapes ($\gamma_i^{(1)}$ is the second angular derivative in a direction of maximum ($i = 1$) or minimum ($i = 2$) curvature of the $\gamma(\theta, \phi)$ surface) and in fact γ itself is not uniquely defined. Now Wulff's construction (fig. 5) involves drawing the radius vector of the $\gamma(\theta, \phi)$ surface at each point on the surface and then constructing the normal plane at that point. The solid enclosed by these planes has the crystal shape: of course, its actual dimensions in any direction are determined by the amount of solid, gravity and other constraints. In high symmetry directions $\gamma(\theta, \phi)$ shows singularities, in the form of cusps, and application of the Wulff construction gives facets. Depending on the depth of the cusps, the facets may intersect or may go continuously into curved surfaces. When we go through the roughening transition, the cusp becomes rounded; there can be no sharp distinction between a rough surface whose average orientation is exactly a high symmetry direction and one whose average is *almost* a high symmetry direction. Following through the Wulff construction shows that the radius of curvature of the surface becomes finite but large at the roughening transition and sub-

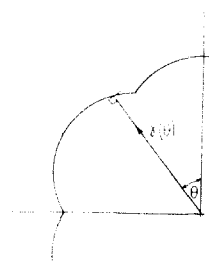


Fig. 5. Illustration of Wulff's construction.

sequently decreases with increasing temperature. Such a transition is obviously very difficult to pinpoint exactly.

In the same way as knowledge of $\gamma(\theta, \phi)$ allows the crystal shape to be deduced, the crystal shape allows $\gamma(\theta, \phi)$ to be calculated provided that the uncertainties involved in the γ^{11} terms are dealt with. The calculation is described in detail by Arbel and Cahn [12], and symmetry can be exploited to remove the ambiguity in the results. Some preliminary results for $\gamma(\theta)$ in the plane normal to (0001) are shown in fig. 6; the scale of the measurements can only be found after taking into account exactly the effect of gravity, and this has not yet been done.

Finally, I should like to mention some other aspects of this work. When we introduce very small amounts of ^3He into the fluid, crystal growth changes quite appreciably. 100 p.p.m. of ^3He (0.01%) is enough to stabilize faceted crystals at all temperatures. Avron has suggested [8] that the ^3He , by remaining in the fluid but bound to the interface, prevents the random fluctuations of the surface. If the ^3He were to move with the surface it would have to do so by diffusion in the liquid, which would quite effectively prevent macroscopic motion.

When the ^3He concentration is higher (about 0.5%) one can see visually that something strange is happening. Faceted h.c.p. crystals grow quite readily at this concentration. On melting them, by reducing pressure, the crystals melt from the inside out, so that the last remaining part of the crystal is the faceted shell (fig. 7). It is difficult to explain this purely on the basis of

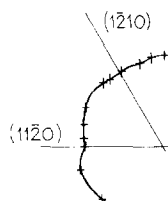


Fig. 6. Preliminary experimental results for $\gamma(\theta)$ in the plane normal to (0001).

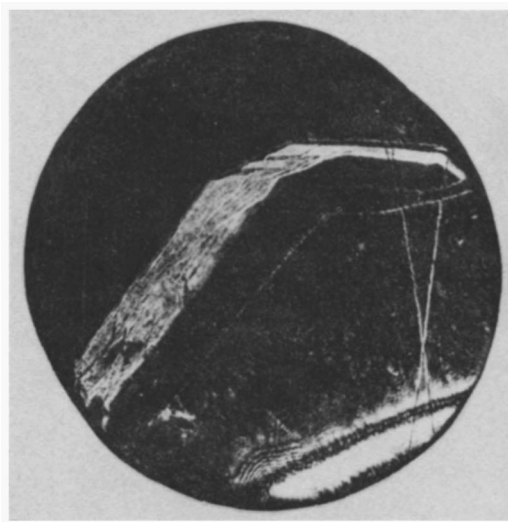


Fig. 7. Dark ground photograph showing the shell remaining as an 0.5% crystal melts.

what is known at present about the ^3He – ^4He solid–liquid phase diagram, and it is almost certainly an indication of some form of surface structure being present. We hope to have some new information on this effect in the near future.

The death of Judah Landau, who inspired much of this work and whose enthusiasm carried it so far, is a great loss to the world of low temperature physics. We shall do our best to continue it with the same spirit.

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