

The Surface Tension of b.c.c. ^3He Crystals.

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Abstract. – We have measured the surface tension γ of b.c.c. solid helium-3 from the visual observation of large single crystals, in equilibrium with their liquid phase, between 0.1 and 0.4 K. This first direct measurement gives a much larger result ($\gamma = (0.060 \pm 0.011)$ erg/cm²) than previously estimated from the maximum temperature at which facets were observed on growing crystals (0.10 K). We propose that quantum fluctuations reduce the step energy and broaden the roughening transition, so that dynamic roughening may occur far below the static roughening temperature.

We report the first direct measurement of γ , the surface tension (or stiffness since we assumed that it is isotropic) of ^3He crystals, between 0.1 and 0.4 K. From the study of the crystallization of ^3He in various porous media, several authors proposed [1] values for γ ranging from 0.02 to 0.25 erg/cm². The large scatter in these results probably arises from a rather poor knowledge of both the geometry of the pores and the crystallization process in them [2]. Thus, a more precise measurement was needed, in order to check the universal relation [3] of roughening. This relation ($k_B T_R = (2/\pi) \gamma a^2$) links the temperature T_R , at which facets appear, to γ and a , the crystal periodicity. It is one of the results of the critical theory of roughening [4, 5], whose main predictions were all found in good agreement with the properties of ^4He crystals [6]. The universal relation therefore seems well established to us. Still, it seemed interesting to check it also in ^3He , since ^3He is actually rather different from ^4He . In a sense it is a more classical substance: liquid ^3He is not superfluid close to its first roughening transition [2, 7]. As in all ordinary crystals, when observing the roughening transition in ^3He , one has to be careful about heat diffusion problems which may hide interface properties. However, from another point of view, liquid ^3He is usually described as

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a Fermi liquid, and the Fermi momentum of ${}^3\text{He}$ quasi-particles seems to be a quantity relevant to the growth dynamics of ${}^3\text{He}$ crystals [8]. An additional reason for considering ${}^3\text{He}$ as an even more quantum system than ${}^4\text{He}$ is the larger zero point motion due to a lighter mass. As a matter of fact, we found a surprisingly high value for the surface tension which seems to contradict the universal relation. In this letter, we first present our method, our experimental technique and our results. We then suggest a possible explanation for the apparent contradiction.

When a crystal is in contact with its fluid phase, and if thermodynamic equilibrium is approached closely enough, its shape is only governed by gravity and surface tension. Indeed, assuming that T and P are very homogeneous and writing the mechanical equilibrium of the interface leads to the Laplace equation $P_S - P_L = \gamma C$, where P_S is the pressure in the solid, P_L the pressure in the liquid, and C is the curvature ($C = 1/R + 1/R'$, where R and R' are the two curvature radii). When combined with the hydrostatic equilibrium in the liquid ($dP_L/dz = -\rho g$) and with the thermodynamic equilibrium at the interface, this relation becomes $(\rho_S - \rho_L)g(z_0 - z) = \gamma C$, where ρ_S , ρ_L are densities and z_0 is the equilibrium height of a flat interface. A well-known consequence is that crystals with increasing size deviate from the spherical shape when they become larger than the capillary length $\lambda = (\gamma/(g\rho_S - \rho_L))^{1/2}$. Since we expected λ to be slightly less than 1 mm in ${}^3\text{He}$, we decided to measure the shape of crystals with sizes ranging from 1 to 3 mm, to fit them with a numerical solution of the Laplace equation and to obtain γ . Such a solution is easy to obtain, if one supposes that γ is isotropic and that the crystal has a vertical axis of revolution symmetry. The first assumption was supported by the previous observation [7] of quasi-circular profiles for smaller crystals⁽¹⁾. The second one seems natural if crystals are freely lying on a horizontal floor.

Of course, the method would never have worked if we had not been able to get a very good temperature homogeneity, despite having windows and the minimum necessary illumination of our cell. Close to the minimum in the melting curve, at 0.32 K, we needed to reduce possible inhomogeneities well below 0.1 mK. Around 0.1 K, where the slope in the melting curve is large and negative, inhomogeneities of about 0.5 μK would have driven our crystals to hot spots in the cell. As shown by fig. 1, our cell is a copper block with sapphire windows. All its pieces are in good thermal contact with a surrounding ${}^4\text{He}$ bath. We obtained very nicely symmetric shapes down to 0.15 K, showing that the temperature was homogeneous enough.

We also had to purify our helium. Indeed, for the first experiments [2, 7], ordinary ${}^3\text{He}$ was used which contained 200 p.p.m. ${}^4\text{He}$; its crystallization was dendritic, and, even after very long relaxation times (more than one day), we observed rather distorted shapes which were probably due to the slight solubility and slow diffusion of ${}^4\text{He}$ in solid ${}^3\text{He}$ [9]. We then used purified ${}^3\text{He}$ with only 5 p.p.m. ${}^4\text{He}$ and assumed that this residual amount was completely adsorbed on the cell walls. Since the cell (0.15 cm^3) contained two sintered copper pieces (fig. 1) with a total surface area of 70 cm^2 , the adsorbed ${}^4\text{He}$ was probably about half a monolayer. Of course, the sintered copper was primarily put to improve the thermalization. The temperature was measured in the ${}^4\text{He}$ bath and its calibration checked against the known ${}^3\text{He}$ melting curve [10].

We usually obtained equilibrium shapes of single crystals as follows. At 0.4 K, the cell was partially filled with solid ${}^3\text{He}$ by slowly pressurizing from the outside. It was then closed with the low-temperature microvalve, and the cell volume was adjusted to obtain the

⁽¹⁾ A 10% anisotropy of the surface stiffness implies the same 10% anisotropy in the curvature radius of a small equilibrium crystal shape; but, with 4-fold symmetry axes, this may be consistent with less than a 1% anisotropy in surface free energy or crystal radius.

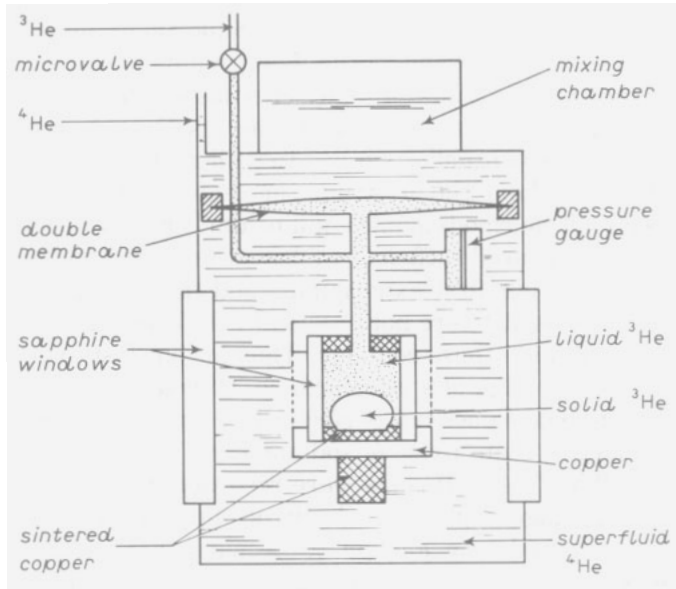


Fig. 1. – The experimental cell, in which ^3He crystals were grown and observed, is immersed in superfluid ^4He . The cell windows are 5 mm apart; the cell section is a square (3.5 by 3.5 mm). The sintered copper allows a good thermalization, but also adsorbs all the residual ^4He impurities. Thanks to the Be-Cu double membrane, when the outside ^4He pressure is changed, the cell volume may vary by 5%. The crystals were kept in the centre of the bottom of the cell by drilling a hole in the sintered copper piece (diameter: 2 mm, depth: 0.1 mm).

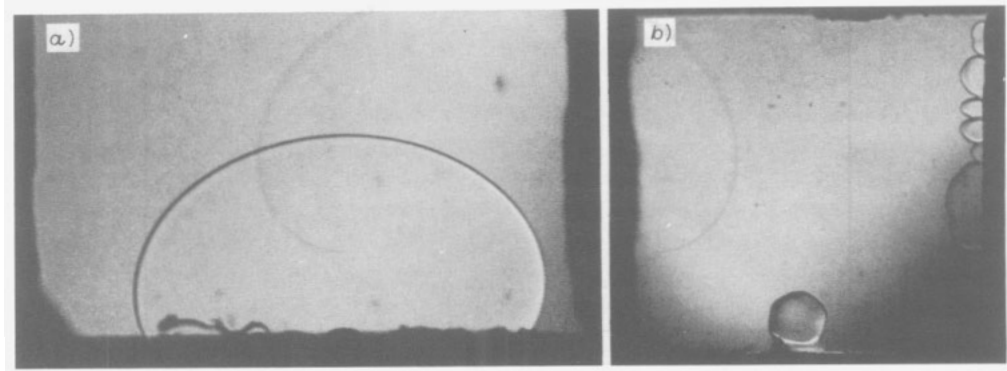


Fig. 2. – *a*) We obtained such equilibrium shapes of ^3He crystals after waiting a few minutes at $T = 0.32$ K but a few hours below 0.2 K, where the latent heat is large and the crystal shape very sensitive to residual temperature gradients. Here $T = 0.32$ K and the total crystal width is 2.6 mm. The crystal slightly escapes from its hole, which produces a slight asymmetry in the lowest part of the profile. We digitized such profiles and obtained the surface tension from a fit with the Laplace equation (see fig. 3). *b*) This faceted crystal was obtained at 0.10 K. It nucleated on the bottom wall. The growth velocity was about $0.1 \mu\text{s}$. The facet radii are about $100 \mu\text{m}$ and the curvature radii at corners typically $10 \mu\text{m}$. From this observation and the fact that we never succeeded in observing facets at higher temperature, we had deduced that the roughening temperature for (110) facets in ^3He was about 0.10 K. However, our measurements of the surface tension now indicate that the true roughening temperature may be much higher.

desired quantity of crystal. A total variation of 5% could be obtained thanks to the upper part which is a Be-Cu double membrane whose inner volume depends on the ^4He pressure. Usually, the first crystallization produced many crystals which nucleated on the walls. By slowly cycling the temperature around 0.32 K, it was easy to help the biggest one to grow and all the others to shrink. Eventually, we had to drill a rather large hole in the centre of the cell (2 mm in diameter) to keep the crystal in the centre and avoid contacts with the side walls. Indeed, as expected if thermodynamic equilibrium is reached, even a 1° tilt of the floor with respect to horizontal appeared sufficient to drive the crystal to the lowest corner of the cell [2]. We had such a tilt in our first experiments and the crystals touched the right wall and the front window. Our results were not drastically different from what we now present, but it was important to eliminate these contacts. Thus for our last experiments, the crystals usually stay on the horizontal edge of a circular hole. Of course this procedure only worked because the solid-liquid interface does not perfectly wet walls; the contact angle seems close to 180° and certainly larger than 150° . A sodium lamp was used to illuminate crystals through infrared and yellow filters. Images were recorded with a simple video system and profiles digitized with an image analyser and microcomputer. After any change in crystal size or temperature we waited long enough to be sure that the relaxation towards the equilibrium shape was completed. This waiting time was typically a few minutes near 0.32 K [8], but about one day at 0.15 K, the lowest temperature at which we succeeded in keeping one large single crystal in the right place of the cell.

Figure 3 shows a typical example of fit between a numerical integration of the Laplace

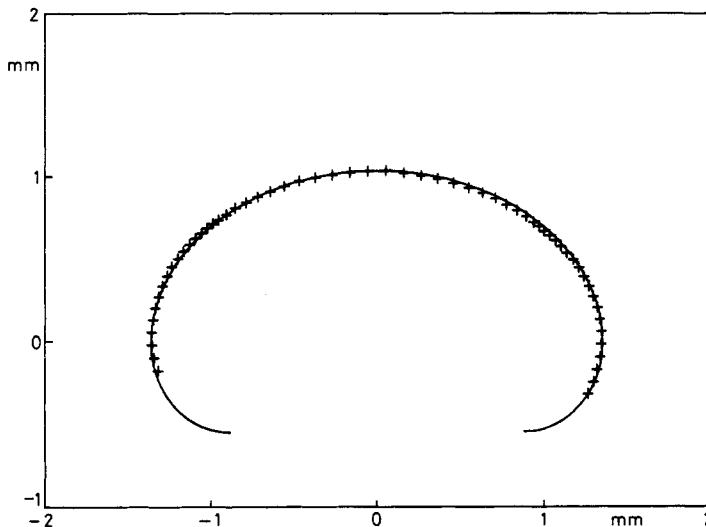


Fig. 3. - As shown by this fit, the equilibrium shape of our ^3He crystal (crosses) is very close to what the Laplace equation predicts (solid line). We have assumed that the surface tension γ is isotropic and that the crystal has a vertical axis of revolution symmetry. In this particular example, $T = 0.32$ K and we found $\gamma = 0.056$ erg/cm 2 .

equation and a digitized profile (we did not use the very lowest part but still show the full theoretical shape down to the points where the slope is horizontal). We found no systematic variation of γ with crystal radius (0.8 to 1.7 mm). Therefore, temperature or concentration gradients were really negligible. The goodness of our fits also proves that the anisotropy of γ is small, as assumed; however, it may actually be responsible for the very slight systematic deviations from the theoretical curve which were sometimes observed on some parts of the

profile. Moreover, these slight deviations may also be due to the contact with the cell floor, which did not always occur on the desired horizontal circle. For example, in fig. 2a), the crystal slightly escapes from its hole on the right side so that the revolution symmetry is slightly broken. Both a possible anisotropy of γ and this anchoring problem of our crystals may be responsible for the rather large dispersion in our final results (fig. 4). On this figure, the 5% error bars represent the sum of errors in the profile measurement, the general calibration of distances and astigmatism, and the fit. The surface tension does not seem temperature dependent (fig. 4). Averaging over all measurements leads to a capillary length $\lambda = (1.03 \pm 0.09)$ mm and to a surface tension $\gamma = (0.060 \pm 0.011)$ erg/cm² (now the error bars characterize the scatter in the results). Our value lies in between the various past estimates [1].

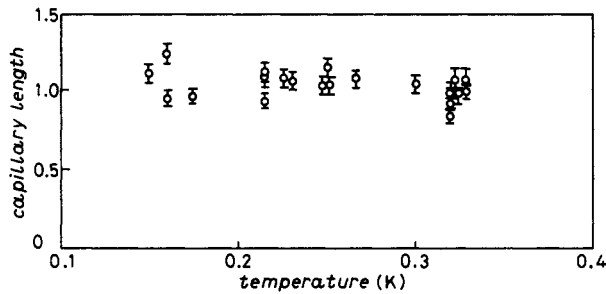


Fig. 4. – The capillary length for solid ^3He is temperature independent and close to 1 mm between 0.1 and 0.4 K. Moreover, we did not find any variation with crystal size. Averaging over all our measurements leads to a surface tension $\gamma = (0.060 \pm 0.011)$ erg/cm².

It is more important to compare our experimental value of γ with the roughening temperature. As previously explained [2, 7], facets are difficult to observe on the equilibrium shapes of ^3He crystals but clearly visible on crystals growing below 0.10 K if their velocity is not too large (less than $1 \mu\text{/s}$ at 0.10 K, for example). From this observation, and a comparison with ^4He , we had proposed [2] that $T_R \approx 0.10$ K for (110) facets in ^3He . Indeed, on slowly growing ^4He crystals, we had seen facets up to 1.26 K, very close to the true roughening temperature $T_R = 1.28$ K [6]. However, the universal relation would then be violated in ^3He : from $T_R = 0.10$ K, and $a = 3.07 \text{ \AA}$, one predicts $\gamma = 0.023$ erg/cm², less than half our experimental value. Of course our measurements do not extend down to 0.10 K, but any critical variation of γ at $T \geq T_R$ would make the disagreement worse (γ increases close to T_R).

At the beginning of our experiment [2], we only had results around 0.32 K and the discrepancy was between an estimate at 0.10 K and a measurement at higher temperature. We thought that perhaps the surface entropy could be large and negative. Supposing that the exchange in the interface was enhanced, we imagined that some magnetic ordering existed in it up to a rather high temperature. The entropy could then be as large as $-k_B \ln 2$ per atom, or -0.10 erg/cm² K for one surface layer, which could double the surface stiffness from 0.1 to 0.2 K. However, we now know that there is no such large variation of γ with temperature. Since we do not see why the universal relation should not apply to ^3He , we are forced to criticize our previous measurement of T_R .

We propose an interpretation based on the difference between the temperature at which a growing crystal roughens and the true equilibrium roughening temperature. When a crystal grows at a velocity v , below T_R , facets disappear [4, 6] when the lifetime of fluctuations with size ξ (the correlation length) becomes larger than the time a/v which is

necessary for the crystal to grow by one atomic layer. Indeed, in such a case, the fluctuations are liberated from the influence of the periodic potential due to the lattice: it is averaged to zero in time by the growth. This effect is known as dynamic roughening [4]. As explained in ref. [4], $\xi \approx k_B T_R / \beta$ (β is the step energy) and $v = k \Delta\mu$ (where k is the growth rate and $\Delta\mu$ the difference in chemical potential across the facet). Moreover, from the diffusion equation which governs the interface motion [4], one finds that the diffusion constant for surface fluctuations is $k\gamma/\rho_S$. Therefore, the criterion for this dynamic roughening is $(\beta^2 a \rho_S \Delta\mu k_B T_R) \approx 1$. Note that this is equivalent to $r_c/\xi \approx 1$, where r_c is the critical radius for the nucleation of terraces. Close to dynamic roughening, the nucleation of terraces generates the surface fluctuations and always dominates the other growth mechanisms. Anyhow, when observing crystals growing at increasing temperature and finite velocity, the facets disappear at $T \leq T_R$, when $r_c = \xi$, not exactly at T_R . Let us try to estimate r_c , *i.e.* $\Delta\mu$. As shown by fig. 2b), we observed facets at 0.10 K on crystals growing at about 0.1 μ /s; the facet radius L was about 100 μ m, much larger than the rough corner radius R (about 10 μ m). We first remark that the growth rate of the facets is much smaller than that of the rough adjacent surfaces. For a stationary growth shape, the difference in chemical potential $\Delta\mu_1$ across the facet has to be much larger than the difference $\Delta\mu_2$ across the corner. Moreover, since the heat conductivity in the solid [11] is large, the difference $\Delta\mu_1 - \Delta\mu_2$ mainly arises from a difference in the effective solid pressure: a stationary shape with an anisotropic growth rate imposes a slight strain in the growing crystal. Since the observed facet size is also much larger than what it should be on an equilibrium shape, the pressure difference across the facet must be very small. This is nothing but saying that T and P are constant everywhere, except inside the crystal corner, where P_S has to be $2\gamma/R$ higher (mechanical equilibrium) and we obtain $\Delta\mu_1 = 2\gamma/\rho_S R$. From this estimate of $\Delta\mu_1$, we deduce that $r_c/\xi \approx (R/a)(\beta^2/2\gamma k_B T_R)$. For crystals growing at such a velocity that $R = 10 \mu$ m, the facets should disappear when $\beta^2 \approx 6 \cdot 10^{-5} \gamma k_B T_R \approx 4 \cdot 10^{-5} \gamma^2 a^2$. In the case of ^4He , β was found [6, 12] to decrease from about $10^{-1} \gamma a$ at $T = 0$ to about $10^{-2} \gamma a$ at $0.8T_R$, and to present the well-known exponential critical behaviour close to T_R . In ^4He , as in all other systems, the dynamic roughening only occurs rather close to T_R . In order to reconcile our measurement of γ with the universal relation of roughening, we need the dynamic roughening to occur in ^3He at less than half the true (static) roughening temperature T_R . This may be possible if the larger zero point motion decreases the coupling of the interface to the lattice; this would decrease the unrenormalized value of $\beta/\gamma a$ at $T = 0$, but mainly broaden the transition. It could also explain why we never observed facets on the equilibrium shapes of ^3He crystals: the ratio of the facet radius to the crystal radius is $\beta/\gamma a$. This is perhaps highly speculative, but, at least, it may explain why the apparent roughening temperature (0.10 K) seems much lower than the true roughening temperature ($T_R > 0.2$ K?). It would be also interesting to look for the (100) and (111) facets, whose roughening temperature should be two or three times lower than for the (110) facet.

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