

The surface of crystalline helium-4

A solid that one can produce by simply applying pressure to liquid helium-4 is an excellent medium for studying the appearance of facets, the kinetics of crystal growth and other fundamental problems of surface physics.

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Although solid helium was first produced over 60 years ago, by Willem H. Keesom at Leiden,¹ it is only in the last few years that physicists have studied the surface of this solid. They have discovered that the surface has remarkable properties of great scientific interest:

► It is extraordinarily pure chemically, and can be made isotopically pure and free of crystal defects.

► Its growth is easily manipulated (as the cover of this magazine indicates) because it is more a mechanical process than a thermal process. In this article we examine these properties and explain the consequent unique opportunities that the helium surface gives us for studying problems that are of general interest in surface physics. Most of the findings that we discuss come from the four countries where research on the surface of solid helium is most active: the United States, the Soviet Union (see figure 1), France

and Israel.

Helium has a unique phase diagram because it is the only element for which liquid is the stable phase at 0 K and atmospheric pressure. To produce solid helium it is necessary to apply a pressure sufficient to force the atoms into a more closely packed arrangement. The properties of both liquid and solid helium are greatly affected by the large zero-point kinetic energy of the helium atoms; this energy is large

because the atoms are light. The potential energy of the solid—due to the interatomic forces—is, as for other elements, less than that of the liquid. However, because of the more open structure of the liquid (that is, because the atoms in the liquid are less confined), the zero-point kinetic energy for the liquid is much smaller than that for the solid. In helium this difference is sufficient to make the total energy of the liquid less than that of the solid,

accounting for the stable liquid phase at 0 K. The pressure required for freezing He⁴ is 25 bars and that for freezing He³ is 35 bars.

Figure 2 is a qualitative phase diagram for He⁴. There are three solid phases:

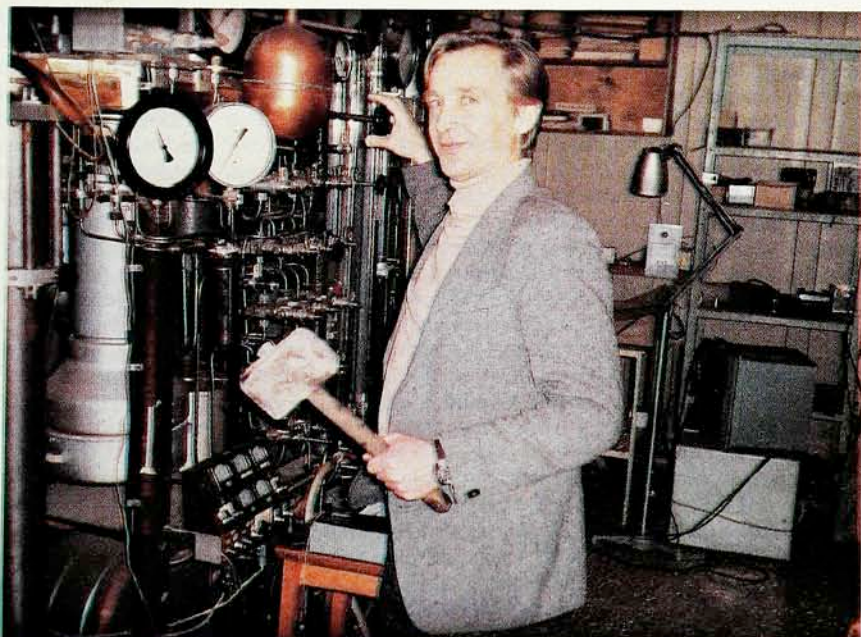
► Hexagonal close-packed, which is the stable phase at low temperature

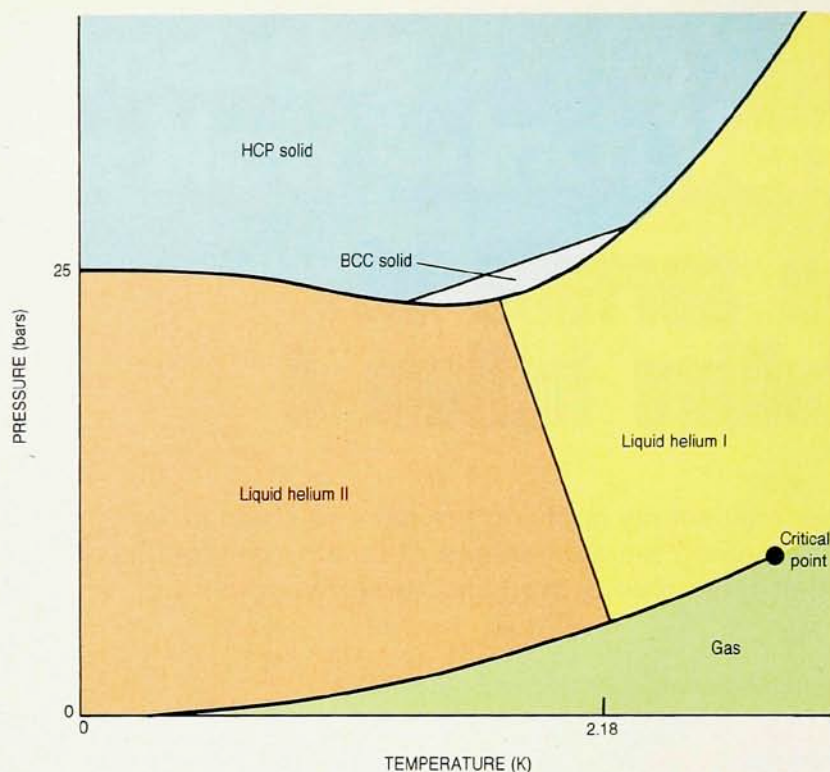
► Body-centered cubic, which occupies a small region of the phase diagram near the melting curve

► Face-centered cubic, which occurs at high pressure and is not included in figure 2.

Aleksander Parshin's low-temperature research lab in Moscow. Aleksander Andreev, melting-freezing wave generator in hand, adjusts a valve.

Figure 1





Phase diagram of He^4 , not to scale. The pressure at the critical point is 2.3 bars and the temperature is 5.2 K. Note that at low temperatures the freezing pressure is almost independent of temperature.

Figure 2

The liquid phase is divided into helium I, which is a fairly normal liquid, and helium II, which is superfluid. The boundary between these liquid phases is called the λ line; it is at 1.8 K when the pressure is near that required for freezing and is at 2.2 K when the pressure is near zero. In contrast to all other elements, helium has a phase diagram with no triple point where liquid, solid and gas phases coexist.

Because pressure is required to produce solid helium, it is impossible to produce a "free surface" of the solid phase—a boundary between the solid and the gas. Thus, when we talk in this article about the surface of solid helium, we always mean the interface between the solid and liquid phases.

Why study the He^4 surface?

One can prepare liquid helium with an almost complete absence of impurities, because all other elements freeze out at higher temperatures. There are techniques available to reduce the con-

centration of the He^3 isotope in the liquid to below 1 part in 10^{12} . Thus, if one produces the solid by applying pressure to the liquid, the liquid-solid surface will be essentially free of impurities. One can grow high-quality crystals of the solid, and the high mobility of the atoms in the solid phase enables one to anneal these crystals to reduce the density of dislocations.

The extreme cleanliness of the solid helium surface makes the study of the liquid-solid interface an attractive field of research. However, at temperatures below about 1 K there are additional reasons for studying this interface. For ordinary substances, when a crystal is grown from the liquid phase, the latent heat of fusion is liberated at the interface, producing a local rise in temperature. For growth to proceed this heat has to be conducted away, through either the liquid or the solid. The growth rate of the crystal is thus controlled primarily by heat conduction in the bulk phases; the actual kinetic processes that occur at the interface are of secondary importance, and can be studied only in especially favorable situations.² For helium the situation is different in two important respects: First, the superfluid has an

extremely high thermal conductivity, so heat generated at the interface is removed very rapidly. Second, at temperatures below about 1 K the entropies of both the liquid and the solid phase are very small. Thus the latent heat of fusion is almost zero and, by the Clausius-Clapeyron equation, the freezing pressure is practically independent of temperature. As a result, we should consider freezing to be essentially a *mechanical* process, rather than a *thermal* process as it is for ordinary materials.

The combined effect of high thermal conductivity and low latent heat is that the growth of a helium crystal is limited primarily by processes occurring at the interface, making the kinetics of growth relatively easy to study.

Crystal growth rate

The rate v_g at which a crystal grows is a function of the difference $\Delta\mu$ between the chemical potentials μ_l and μ_s of the liquid and solid phases. The growth coefficient K is defined by

$$v_g = K \Delta\mu$$

The growth coefficient gives information about the nature of the surface. A crystal surface may be either flat and smooth on an atomic scale—a facet—or rough. A rough surface will have a high growth coefficient because it will have many places where an extra atom can be added. Growth is difficult for a smooth surface because atoms can be added only by the nucleation of an entirely new layer of atoms or by spiral growth around screw dislocations that intersect the surface. This leads naturally to the question, is the surface of solid helium at low temperatures rough or smooth? The general idea that at low temperatures all systems should tend toward highly ordered states suggests that the surface should be smooth. On the other hand, Andreiev and Aleksander Parshin argued that even at zero temperature, the quantum mechanical zero-point motion of the atoms at the surface may be sufficient to destroy the facets and turn them into rough surfaces.³ We will discuss the validity of this idea later.

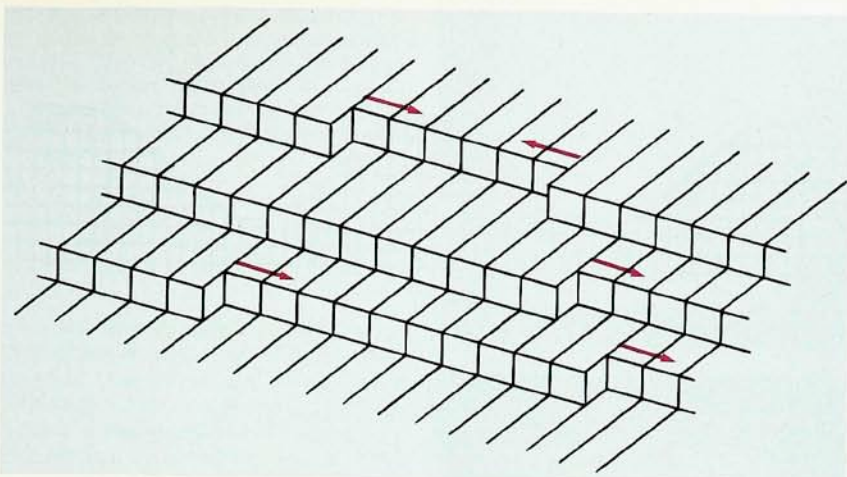
Andreiev and Parshin also put forward the radical idea that the growth coefficient of a rough surface at zero temperature should become infinite.

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This prediction implies that there can be steady-state growth of the interface even in the absence of a chemical potential difference. Their idea was based on a specific model of the interface. As figure 3 indicates, a rough surface has many steps running across it, and these steps contain kinks—they are not straight. Andreev and Parshin argued that these kinks should act as elementary excitations and propagate freely across the surface. Because a moving kink transfers mass from the liquid to the solid, freely propagating kinks correspond to a stationary state of the system in which the solid grows without any dissipation at the interface and without any difference between the chemical potentials of the liquid and the solid.

Andreev and Parshin predicted that because of the very high growth coefficient the surface of solid helium should feature a new type of wave that cannot exist at ordinary interfaces. Figure 4 shows this wave schematically. Consider a solid surface that initially has hills and valleys and is at rest (figure 4a). To lower the surface energy, which is proportional to the area of the curved surface, and the gravitational energy, which is lowest for a horizontal surface, the peaks of the solid begin to melt and the liquid in the valleys begins to freeze. The surface of the solid quickly becomes flat (figure 4b). However, at this stage currents are still flowing in the liquid due to the material that melted, and the inertia of these currents causes the melting and freezing to overshoot (figure 4c). Recall that the liquid is superfluid so that the currents are not damped by viscosity. The cycle then repeats itself, giving a wave motion.

These waves, called melting-freezing waves, were observed in 1979 by Konstantin Keshishev, Parshin and Aleksei Babkin.⁴ The waves can be generated "professionally" by displacing a point on the surface by an electric field, or in a more amateurish way by kicking the cryostat! Figure 5 shows photographs of waves obtained by the second method. Note that these waves are different from the well-known Rayleigh waves that propagate on the surfaces of ordinary solids. In a Rayleigh wave, atoms in the region of the solid near the surface move in elliptical



Steps and kinks on the surface of a crystal. When the kinks move in the direction of the colored arrows, atoms are transferred from the liquid to the solid.

Figure 3

orbits; in a melting-freezing wave, atoms in the solid do not move at all except when they melt and enter the liquid, as indicated in figure 4.

Limits on interface motion. The frequencies used in the first experiments with melting-freezing waves ranged up to about 3 kHz. It seemed remarkable that a crystal could melt and freeze in a reversible and nearly dissipationless way on such a short time scale. However, it now appears that melting and freezing can occur up to much higher frequencies. Bernard Castaing, Sebastien Balibar and Claude Laroche⁵ showed this in experiments at the Ecole Normale Supérieure in Paris using ultrasonics to study the motion of the surface at 10^6 Hz. Since then, several groups⁶ have studied melting and freezing at frequencies up to 10^{10} Hz. Their experiments show that the high mobility of the interface persists even at that frequency.

In addition to considering the maximum frequency with which the interface can move, we may also ask about the maximum velocity of growth. In a recent experiment at Brown University, Michael Graf and Maris⁷ grew solid helium crystals at rates as high as 1200 cm/sec. For growth velocities up to a critical value v_c of about 500 cm/sec, the growth remains ideal—that is, the chemical potential difference $\Delta\mu$ required to drive the growth is extremely small. Above the critical velocity the growth process rapidly becomes much more dissipative of energy, just as the flow of superfluid helium through a tube does above a critical velocity.

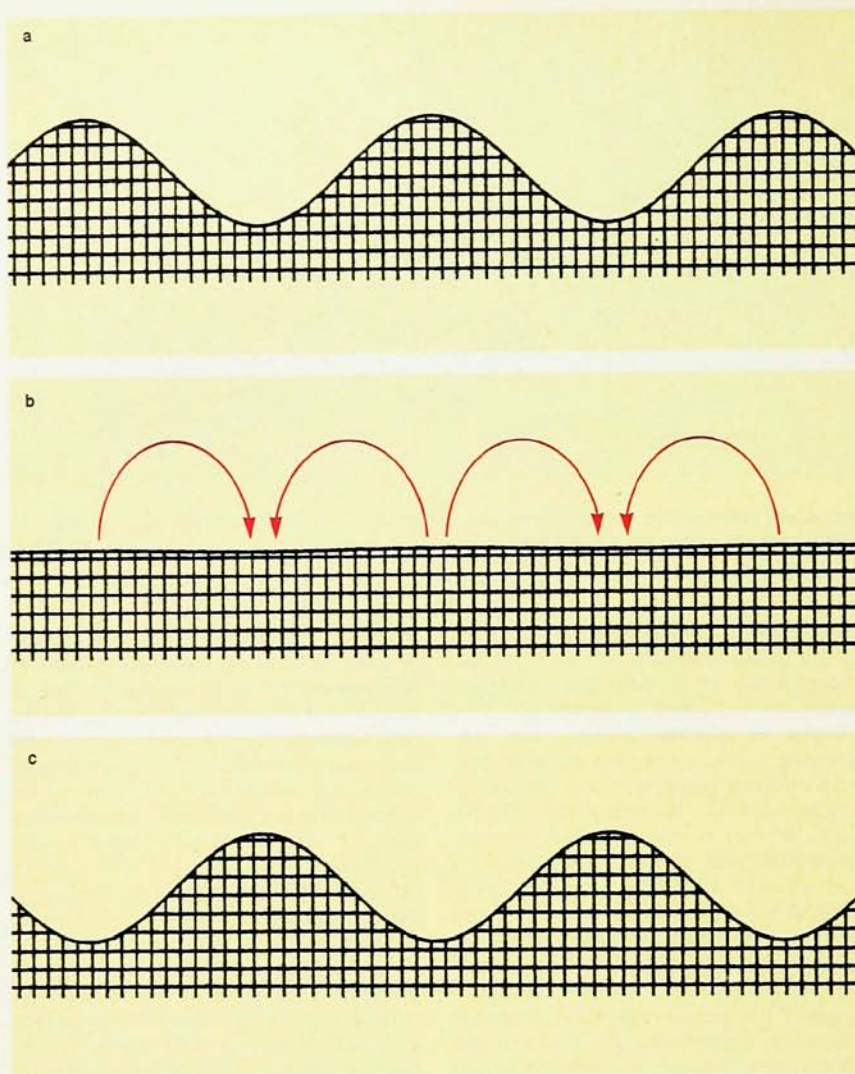
The microscopic origin of the critical velocity for the surface of solid helium is not yet known. However, it is clear on very general grounds that a critical velocity must exist. At the most funda-

mental level we can regard the growth of solid helium as the deformation of the quantum state of the system from a liquid to a solid configuration. When this deformation proceeds slowly, the system will remain in the ground state, while the character of this state changes from liquid to solid. Above a certain rate, however, nonadiabatic processes will begin to occur with appreciable probability, and the growth process will be dissipative and irreversible.

At finite temperatures the thermal phonons and rotons in the liquid and solid damp the motion of the interface and reduce the growth coefficient K . Several experiments have focused on this damping, and the way in which the thermal excitations damp the interface is fairly well understood.⁸ It is clear that when a phonon or roton is reflected from a moving interface it undergoes a Doppler shift and can therefore absorb energy from the interface. The phonons or rotons possibly interact also with the moving kinks on the interface. At high temperatures the growth rate eventually becomes so small that melting-freezing waves are overdamped oscillators. Under these conditions, when the surface is perturbed it simply relaxes back to a flat and horizontal configuration, and does not oscillate. However, even in this case the time the crystal takes to reach its equilibrium form is much less than the corresponding time for a crystal of an ordinary material.

Facets

Our discussion so far has focused on atomically rough surfaces. Experiments at low temperatures show that the surface of a helium crystal consists of both rough and smooth (faceted)



Explanation of melting-freezing waves. **a:** A solid surface with mountains and valleys. **b:** The mountains melt and the liquid in the valleys freezes, producing a flat surface. The inertia of the currents (arrows) in the liquid causes the system to overshoot, producing the shape shown in **c**. The system then reverses its motion and returns to the configuration shown in **a**.

Figure 4

regions. The way in which the facets appear and grow is of great interest, and was first studied in a series of experiments in Paris by Balibar and his coworkers and in Haifa by the group of Steven Lipson and the late Judah Landau.

At temperatures above 1.28 K the entire surface of a helium crystal is rough. Below this temperature, which we call T_c , facets appear normal to the c axis of the crystal.⁹ In the standard notation for hexagonal crystals these are (0001) faces. These facets grow as the temperature is lowered. At a temperature T_a of about 1.0 K new facets appear on a set of six faces perpendicular to the c axis. These faces are (1100) surfaces. At a temperature T_s of about 0.36 K a third type of facet appears¹⁰ on faces that are of orientation (1101).

The cover shows helium crystals at a temperature below T_s . The three different types of facet are visible. The temperatures T_s , T_a and T_c at which faces of the crystal change from smooth to rough as the temperature is raised are called roughening temperatures.

At the phenomenological level, the existence or nonexistence of facets is determined by the way in which the surface free energy varies with the orientation of the crystal surface. The simplest case to calculate is the thermodynamic equilibrium shape of a crystal in the absence of gravity; this approximation is reasonable for small crystals. The surface free energy F_s of a crystal is

$$F_s = \int_S \alpha(\hat{n}) dS$$

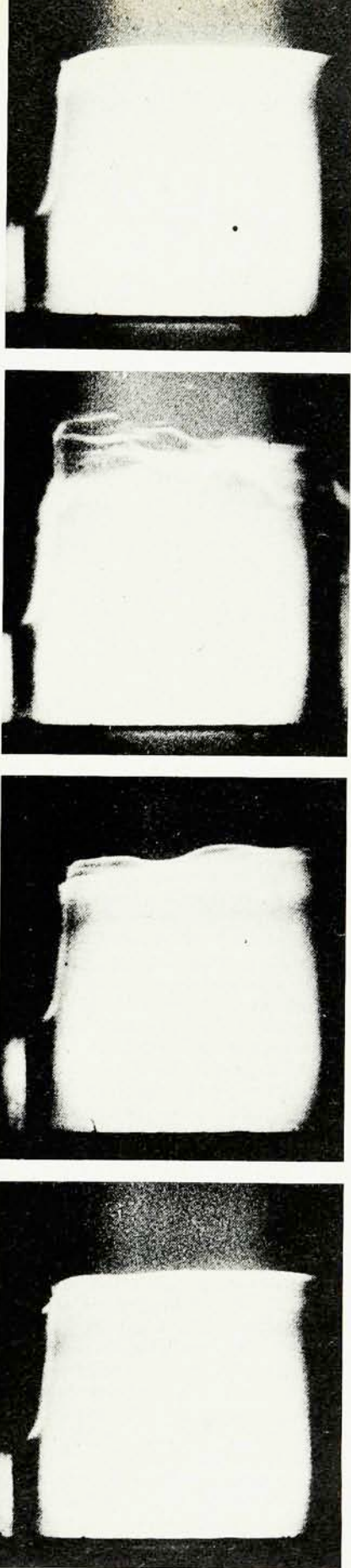
The integral is over the surface of normal $\hat{n}$, and $\alpha(\hat{n})$ is the free energy per unit area for that surface. At equilibrium the crystal takes on a shape such that its free energy F_s is minimized subject to the constraint that the total volume of the crystal has a certain value. One can solve this variational problem geometrically by means of the Wulff construction, a geometrical algorithm that yields the shape of the lowest-energy crystal.² This construction shows that in general, if the surface free energy α is a smoothly varying function of the orientation $\hat{n}$, the surface of the crystal will be rounded and there will be no facets. Facets occur when the surface free energy $\alpha(\hat{n})$ has a minimum value for some particular surface orientation and increases rapidly when one goes away from this orientation—that is, when a polar plot of the surface free energy $\alpha(\hat{n})$ has a cusp in some direction.

We can also view the roughening transition at a more microscopic level, in terms of fluctuations occurring at surfaces. At 0 K a facet is perfectly ordered and smooth. As the temperature is raised, thermal fluctuations give rise to vacancies in the surface layer; occasional extra atoms are also added to the surface. The numbers of these vacancies and extra atoms increase until at the roughening temperature T_R the long-range order of the surface disappears.¹¹

One can view the same transition from the high-temperature side, considering what happens when a rough surface is cooled toward T_R . Because of the high mobility of a rough surface, the fluctuations in this case will be thermal melting-freezing waves. There is a competition between these fluctuations, which tend to delocalize the interface, and the periodic potential of the solid normal to the interface, which favors an interface anchored to a high-symmetry plane of the solid. When the temperature is lowered to the roughening temperature T_R , the periodic potential wins and the surface becomes pinned.

Near the roughening temperature the shape of the crystal exhibits critical behavior. At Ohio State University,

Melting-freezing waves on the surface of solid helium. The top photo shows the surface at rest. The next photo shows the surface after the cryostat was tapped. The last two photos show progressive damping of the waves. (Photographs courtesy of Konstantin Keshishev.) Figure 5



Ciriyam Jayaprakash, William Saam and Stephen Teitel have shown that the same critical properties appear in a wide class of interface models.¹² The three most important of these properties are the following:

► The curvature of the surface below the roughening temperature T_R is zero and above the transition jumps to a finite value given by

$$a^2(\rho_s - \rho_l)(P_l - P_0)/\pi k_B T_R \rho_l \quad (1)$$

Here a is the spacing of crystal planes parallel to the facet plane, ρ_s and ρ_l are the densities of solid and liquid and $(P_l - P_0)$ is the pressure of the liquid above the equilibrium freezing pressure P_0 for a flat interface at the same temperature. This jump is the analog of the jump in superfluid density that occurs at the Kosterlitz-Thouless transition in thin superfluid films (see the article by William Glaberson and Klaus Schwarz on page 54).

► As the temperature increases toward the roughening temperature T_R from below, the length L of a facet tends to zero according to the law

$$L \propto \exp[-A/(T_R - T)^{1/2}]$$

Here A is a constant.

► Consider a facet that is in the plane $z = z_0$. At the boundary between the facet and the rough surface surrounding it, there is no discontinuity in the orientation of the surface. Theory predicts that the surface at a distance r outside the edge of the facet is described by

$$z = z_0 - Br^{3/2} \quad (2)$$

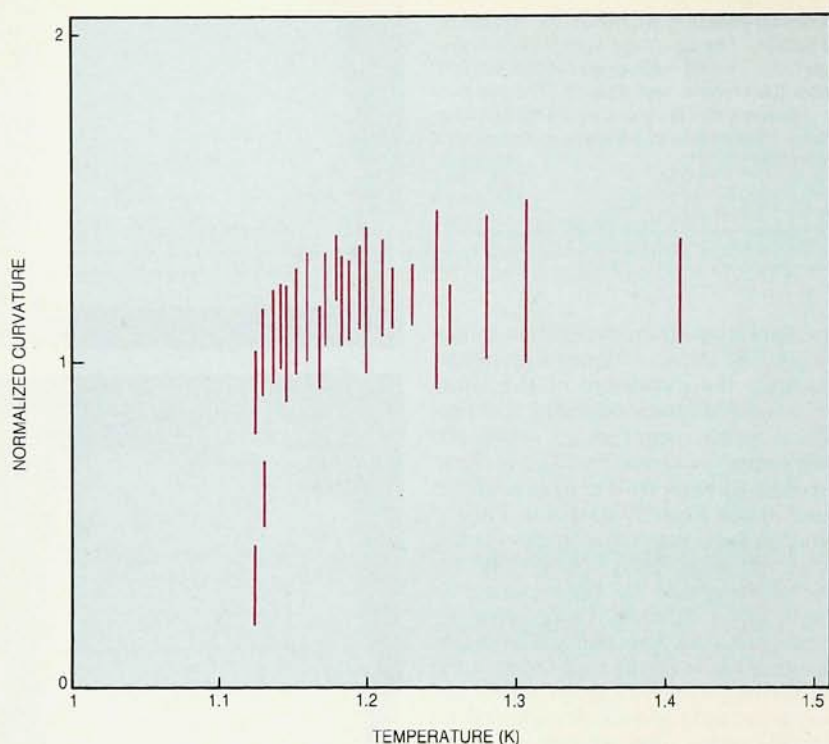
The coefficient B is temperature dependent.

Advantages of helium. The above results are general, and so should apply to other crystal surfaces as well as to helium. However, for the reasons we have discussed already, the critical behavior near a roughening transition will be very hard to observe for ordinary crystals. Because of their significant latent heat of fusion, ordinary crystals take a very long time to reach the shape that is characteristic of true thermodynamic equilibrium—the shape that minimizes the surface energy.

This problem is greatly reduced for helium at low temperatures, and exper-

imenters have already carried out some tests of the theory. Figure 6 shows an example: the curvature of the solid-helium surface, normalized by the theoretical value (equation 1) above the roughening temperature T_R , as measured by Etienne Wolf and his collaborators at the Ecole Normale in Paris.¹³ One can see a jump that is close to the expected magnitude. Although the crystal does take on the equilibrium shape fairly quickly, these measurements are still very difficult to make. The changes in shape that occur at the roughening temperature are small, and they occur only in a small region of the crystal surface. For example, the jump in curvature occurs at just one point. A curvature measurement always probes a finite area of the surface, and hence tends to smear out the transition. Nevertheless, it is likely there will be more accurate tests of the predicted critical behavior in the next year or two.

There should also be critical behavior of the dynamic properties of the interface, such as the growth coefficient K . At temperatures far below the roughening temperature, the growth coefficient is much smaller for a facet than for a rough surface. For a facet there are two possible growth mechanisms to consider: The first is the well-known "spiral" growth around screw dislocations that intersect the surface. This appears to be the dominant growth mechanism¹² at temperatures below 0.5 K. In this temperature range the growth rate decreases as the temperature goes up. It is believed that the growth rate decreases with temperature because phonons and rotons collide with the steps, limiting the velocity with which the steps move around the screw dislocations. The other growth mechanism is the two-dimensional nucleation of new solid layers. If we assume that this is a thermally activated process, the growth rate due to this mechanism will increase with increasing temperature. As the temperature increases through the roughening temperature there must be a transition from this type of growth to the growth characteristic of a rough surface. The results of experimental studies of this transition are in agreement with a



Curvature of the solid-helium surface in the (0001) direction (the c axis) as a function of temperature near the roughening transition.¹³ The plotted values are normalized by the theoretically predicted curvature above the transition, as given by equation 1. Figure 6

renormalization-group theory for the growth coefficient in this region.¹²

Only three faceting transitions have been observed so far. The equilibrium shape of a solid helium crystal at zero temperature remains an intriguing question. In their original paper, Andreev and Parshin proposed that quantum fluctuations, or zero-point motions, could, if large enough, keep some or all of the surface in a rough state. It is now clear from experiments that at a fairly low temperature such as 0.1 K a large part of the surface of a helium crystal is faceted. In addition, a renormalization-group calculation shows that a solid's periodic potential should always lead to faceting, regardless of the strength of quantum fluctuations.¹⁴ Thus, as the solid approaches zero temperature either the existing facets should grow to cover the surface completely or new faceting transitions should occur on faces of lower symmetry. However, no new transitions have been detected by direct visual observation¹⁰ down to 70 mK, and there is clear evidence from many experiments that a significant portion of the interface is still rough in this temperature range. It would obviously be worthwhile to continue the study of the surface to much lower temperatures to look for further transitions and to measure the rate at which the fraction of the surface that is rough decreases as the temperature goes down.

Many of the phenomena we have

described should also appear in experiments with liquid and solid He³, but much lower temperatures will be required. Spin disorder in solid He³ keeps the entropy large down to the magnetic ordering temperature of about 1 mK. Below this temperature it should be possible to propagate melting-freezing waves, and the study of these waves and their damping may give useful information about the magnetic state near the surface. Experimenters have detected¹⁵ only one roughening transition in He³—at 80 mK—and presumably there are other transitions to be found at lower temperatures.

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