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SURFACE PHENOMENA IN QUANTUM CRYSTALS

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I Introduction

The ability to preserve a definite shape is the most obvious property that distinguishes a solid from a liquid. Under ordinary conditions no internal motions take place in a solid and lead to changes in the relative placements of its parts, and hence to changes in its shape. Capillary phenomena, which are so typical of liquids, are therefore usually not observed in crystals.

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Of course, the outer shape of a body can be altered not only by external motions. Thus, in the course of melting or crystallization the shape of the crystal changes because the particles go over from one phase to another. An important factor is that under conditions close to equilibrium these processes are usually exceedingly slow; in practice, the crystal simply does not have time to assume an equilibrium shape within a practicable time interval.

The physical reason why crystals grow too slowly under ordinary conditions is the following. In crystallization, as in any first-order phase transition, the states of the two phases are separated from each other by some energy barrier that ensures the stability of each of the phases. For the phase transition to take place at a certain finite rate, it is necessary to disturb in one way or another the phase equilibrium. As a result, the phase transition is always accompanied by energy dissipation, and it is this which limits, in final analysis, the rate of establishment of the phase equilibrium, and in particular the rate of establishment of an equilibrium shape.

The energy dissipation that accompanies the phase transition is determined by the particular crystallization mechanism, which is dictated in turn by the interphase surface. This group of problems is the subject of an extensive literature (see the review articles [1-3]). From the classical point of view, a macroscopically homogeneous surface of a crystal that is at equilibrium with a liquid or a vapor can be atomically smooth or atomically rough. A rough surface is characterized by a high concentration of various types of surface defects, such as steps, kinks, adatoms, and others. An atomically smooth surface can be regarded, with a certain degree of arbitrariness, as a two-dimensional crystal with a small number of defects, while an atomically rough surface can be regarded as a two-dimensional liquid. Naturally, such a liquid can exist in thermodynamic equilibrium only at high enough temperatures. With decreasing temperature this liquid, like all ordinary three-dimensional liquids, should freeze, i.e., turn into a two-dimensional crystal. The semi-empirical criterion whereby a surface is classified as being of one type or the other (the Jackson criterion) is the absolute value of the transition entropy ΔS , i.e., the difference between the entropies of the two phases in contact per particle. The case $\Delta S \gtrsim 1$ corresponds to an atomically smooth surface, while $\Delta S \lesssim 1$ to a rough one. At sufficiently low temperatures a classical crystal can be in equilibrium only with a vapor, whose

entropy per particle increases without limit with decreasing temperature, and consequently the crystal surface should be atomically smooth.

The growth of a crystal with an atomically smooth surface proceeds via thermally activated formation of nuclei of new atomic layers (we are not considering here growth mechanisms due to certain specific defects, such as dislocations, since we are dealing here with the surface of an ideal crystal). Such a process involves the surmounting of very high potential barriers, and therefore the growth rate of a crystal with an atomically smooth surface is usually vanishingly small if the deviation from equilibrium is slight.

An atomically rough surface is characterized by a large number of "landing points," i.e., empty sites whose occupation does not lead to a substantial increase of the surface energy. Under quasi-equilibrium conditions, such as surface ensures the possibility of continuous growth. One should expect in this case the dependence of the growth (or melting) rate on the difference $\Delta\mu$ of the chemical potentials of the two phases to be linear:

$$V = K\Delta\mu \quad (1)$$

where K is the so-called kinetic growth coefficient.

A rough estimate of the minimum possible value of the shape relaxation time for a classical crystal with an atomically rough surface can be obtained from the following simple considerations. Let the difference $\Delta\mu$ between the chemical potentials of the two phases be of the order of the characteristic energy per particle: $\Delta\mu \sim T_m$ (we assume that the second phase is a liquid). The crystallization rate, obviously, does not exceed the average thermal velocity $V_l \sim \sqrt{T_m/m}$. Assuming that $\Delta\mu$ and V are connected by the linear relation $V = K\Delta\mu$ down to arbitrarily small values of $\Delta\mu$, we obtain for the kinetic crystallization coefficient K the estimate

$$K \lesssim (mT_m)^{-1/2} \quad (2)$$

Furthermore, if the crystal shape deviates greatly from equilibrium, then $\Delta\mu \sim (\alpha/R)a^2$, and at our accuracy we can put $\alpha \sim T_m/a^2$, where α is the surface energy, a is the interatomic distance, and R is the characteristic dimension of the crystal. From this we get for the

shape relaxation time $\tau \sim R/V \approx (R^2/a)\sqrt{m/T_m}$. It is clear even from the very derivation of this relation that the obtained estimate is certainly undervalued and can be regarded only as the classical lower bound of the time τ .

Besides the restrictions imposed by the fact that the kinetic coefficient K is finite, frequently restrictions that are no less substantial follow from an analysis of the heat and mass transfer processes that accompany the phase transition. Thus, if the heat of the transition is not anomalously small and the thermal conductivity is not anomalously high, then similar reasoning yields $\tau \sim (R^3/a^2)\sqrt{m/T_m}$.

We note finally that to obtain a truly equilibrium crystal shape in a real experiment it is necessary to ensure an exceedingly high homogeneity of the temperature field and of the internal stresses in the crystal. Thus, for a maximum permissible temperature difference ΔT in the crystal, under the same assumptions as before, we have $\Delta T \ll (a/R)T_m$. The foregoing arguments demonstrate quite clearly how difficult an experimental problem is the production of a crystal having an equilibrium shape, i.e., a shape determined by its surface energy in accordance with the Wulff theorem [4].

In quantum crystals, and primarily in crystals of helium isotopes, the situation is entirely different. Firstly, these crystals can stay in equilibrium with the liquid down to absolute zero. Next, at sufficiently low temperatures, the heat of melting is very low and the thermal conductivity is high. The situation is particularly favorable in the case of He^4 in the superfluidity region. In the case of He^3 , interest attaches in this sense, first, to the region near the minimum on the melting curve (0.3 K) and second, to the temperature region of the order of 1 mK. Under these conditions the main factor that limits the shape relaxation rate is the kinetic growth coefficient K . It turns out, however, that it is precisely in quantum crystals that a situation is possible wherein K increases without limit with decreasing temperatures [5].

In fact, the freezing temperature of the two-dimensional liquid referred to above is lowered, generally speaking, by the quantum effects. Moreover, if the amplitude of the zero-point oscillations in such a liquid is large enough, the liquid state can be preserved down to absolute zero, in exactly the same manner as liquid helium at low pressures. In other words, the atomically rough surface can remain in the rough state down to absolute zero. Of course, such a surface will

no longer be rough in the usual classical meaning since, in accord with the Nernst theorem, its entropy should vanish at $T=0$. The surface of a quantum crystal can thus be in a special "quantum rough" state.

At absolute zero, all the "roughnesses" in this state should become delocalized and collectivized, they can move only in strictly coherent fashion, in exactly the same manner as the particles of an ordinary superfluid liquid move. This means, in particular, that at absolute zero the growth and melting of a crystal having such a surface can proceed in a strictly nondissipative manner, i.e., the growth coefficient K becomes infinite. In analogy with superfluidity, we can call such a process "supercrystallization" (or "supermelting").

All the foregoing means that in quantum crystals, primarily in He^3 crystals, there can be realized, at least in principle, conditions under which the crystal assumes its equilibrium shape rapidly enough. Such a situation uncovers most extensive possibilities of research into the surface phenomena in crystals, including phenomena heretofore regarded as typical only of liquids.

Surface phenomena in helium crystals have been under intensive study in recent years, both experimental and theoretical. In this article we attempt to report as fully as possible the result of this research. We note beforehand that the most interesting of these results is the existence of weakly damped surface oscillations due to periodic melting and crystallization, wherein the bulk crystal is hardly deformed and remains immobile [6, 7]. In the presence of such oscillations the crystal surface has the appearance of the surface of an ordinary liquid on which a capillary wave propagates. These oscillations—capillary-crystallization waves—can have a macroscopic amplitude limited only by the dimensions of the crystal itself.

It is quite evident that this phenomenon cannot be explained from the classical viewpoint. In fact, the existence of weakly damped waves means that the energy dissipated within one period is much lower than the total energy of the oscillations. An estimate of the energy dissipation due to the finite value of the growth coefficient shows, in accord with (2), that in the classical case this condition is not satisfied for any wavelength all the way to atomic. To understand surface phenomena in He^4 crystals it is thus necessary to invoke new, essentially nonclassical concepts concerning the structure of the surface and the crystallization mechanisms.

II Methods of Growing Helium Crystals and Distinguishing Features of Their Growth at Temperatures Above 1.2 K

Solid helium has no equal as an object for the study of crystal-surface properties. By varying the temperature within a relatively small range (from several tenths of a degree to several degrees) it is possible to track all the distinguishing features that are governed by the surface structure of the crystal and are typical of classical solids. Moreover, at temperatures lower than 1 K, phenomena that have no classical analogs are observed, in which the quantum nature of helium is manifested. The optical transparency of helium determines to a considerable degree the methods used to investigate the crystal surface. Despite the additional technical difficulties that arise in the construction of optical cryostats designed to operate at relatively high pressures (25 atmospheres and more), optical methods are most preferable in a number of cases.

A characteristic feature of working with solid helium is that the first and one of the most crucial stages of the experiment is the process of growing the specimen. In those cases when high quality of the investigated crystals must be ensured, an essential role is played by the choice of the specimen growth procedure. This procedure is determined primarily by the phase-diagram region in which it is proposed to carry out the various measurements.

The first solid-helium specimens were obtained by Keesom [8] in 1926. The thermodynamic parameters along the melting curve of He⁴ were also first measured at that time. It is quite remarkable that, even in these first experiments, all-glass apparatus intended for visual observations was used (Fig. 1). The helium was pumped by a compressor with a mercury piston into a test tube located inside three incompletely silvered Dewar vessels. As a result, Keesom had to examine the content of a thick-wall glass test tube (capable of withstanding a pressure up to 250 atm) through narrow slits in three Dewar vessels, a layer of boiling air, and two layers of boiling helium. This, of course, made observation of a transparent substance highly inconvenient. It is not surprising that it was practically impossible to observe under these conditions the boundary between liquid and solid helium (at almost equal density of the two phases). In Keesom's words "... there is nothing peculiar to be seen in the helium; no

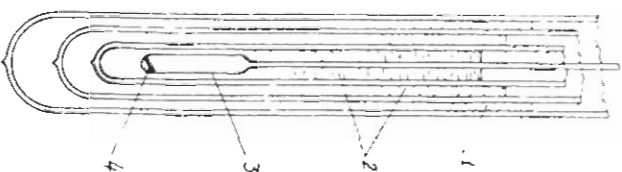


Figure 1 Helium-solidification observation conditions in Keesom's experiments [8]: 1—liquid air, 2—liquid helium, 3—crystalizer, 4—magnetic stirrer.

surface of demarcation between solid and liquid... Helium solidifies to a homogeneous transparent mass. That it is a crystalline mass seems to follow from the fact that the melting curve is sharply defined."

Only once could it be seen how a magnetic stirrer (a piece of iron wire set in motion by an external magnet) dragged behind it a block of solidified helium several millimeters in size, observable only because of the intrusion of extraneous contaminating particles. Keesom's experiments were thus the first attempt at visual observation of the solidification of helium. It should be noted that the crystallization method used in that experiment, known as the "blocked-capillary method," its obvious simplicity notwithstanding, has a major shortcoming. The onset of the crystallization is accompanied in this case by blocking of the working volume, and the succeeding sample growth takes place at constant volume. In view of the appreciable change of the pressure in the course of the growth process, due to the

difference between the densities of the liquid and solid phases, this method is not suitable in principle for growing single-crystal samples.

As a rule, the samples obtained in this manner have a polycrystalline structure. Nonetheless, for more than thirty years, starting with Keesom's first investigation, the blocked-capillary method remained the only way of obtaining solid helium.

Shal'nikov [9] was the first to pay serious attention to the quality of the grown crystals. The very primitive apparatus used in his work was so constructed that the conditions for visual observation of the solidification process were considerably simplified (Fig. 2). The glass

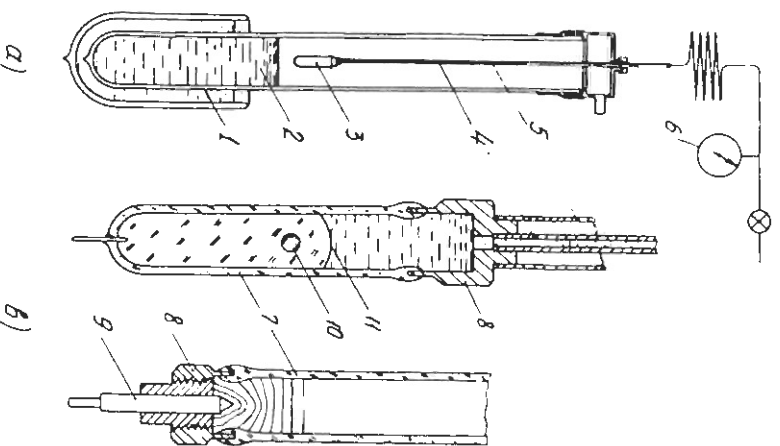


Figure 2. Shal'nikov's apparatus for the observation of the crystallization of helium [9]. a—Experimental setup, b—ampoule for crystal growth: 1—liquid nitrogen, 2—liquid helium, 3—ampoule, 4—high-pressure capillary, 5—vacuum jacket, 6—manometer, 7—glass, 8—ferrocene, 9—copper heat lead, 10—steel ball, 11—interphase surface.

ampoule in which the samples were grown was placed over the surface of liquid helium in an uninsulated Dewar vessel partially immersed in liquid nitrogen. The samples were therefore viewed through only three completely transparent glass walls. Helium gas at a pressure of 25 atmospheres and more was fed into the ampoule through a capillary placed inside a vacuum jacket; this made it completely impossible for solid helium stoppers to form in the path to the ampoule. This vacuum tube served simultaneously as a rod with which to displace the ampoule along the temperature gradient that was established in the cryostat. With the ampoule constantly immersed in the Dewar vessel, it was easy to observe the onset and the subsequent growth of the solid phase produced in the lower part of the ampoule. The boundary between the liquid and solid helium was perfectly visible, and could be easily photographed if the illumination and the contrast were suitable (Fig. 3). For demonstration purposes, a small steel ball was placed inside the ampoule and could be displaced with a magnet. By increasing or decreasing the pressure it was easy to

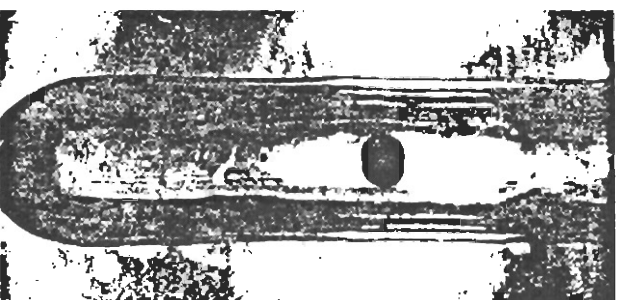


Figure 3. Interface of liquid and solid helium (photograph)

regulate the position of the boundary and to maintain it at the desired level. The same results could be obtained by varying the temperature of the ampoule as it was displaced relative to the helium level in the cryostat.

In these experiments, the observation of the solidification of He^4 and He^3 were carried out in the temperature interval 1.2–4.2 K. It was established that the character of the crystallization is determined primarily by the thermal conductivity of the liquid phase and by the rate of the process itself. Depending on these two factors, several different types of crystallization are possible.

1. At a sufficiently rapid increase of the pressure* the solidification is instantaneous in the entire volume of the ampoule. The produced transparent solid phase, outwardly resembling wet snow, has a finely crystalline structure. By increasing the pressure it is possible to recrystallize this sample and make it transparent as a result. It must be noted that an increased tendency to form a finely crystalline structure is a distinguishing feature of helium of insufficient degree of purity. To all appearances, all impurities that solidify at helium temperatures and are in the liquid helium in a suspended state form numerous crystallization centers.

2. When He^4 solidifies below the λ point** the decisive role is assumed by the anomalously high thermal conductivity of the superfluid liquid phase. In the absence of temperature gradients, even if the crystallization rate is insignificantly low, the formation of the solid phase begins as a rule in several arbitrary places. In this case, simultaneous growth of several transparent crystals is observed; they are nearly spherical in shape and fill gradually the entire volume of the ampoule. That part of the liquid which is located in the lower part of the ampoule is then blocked and has a high probability of remaining unsolidified. The samples grown in this manner have, to all appearances, a block structure. While perfectly transparent, they have a highly uneven hilly surface.

3. A feature of liquid He^3 and He^4 above the λ point is a low thermal conductivity, so that it is quite difficult to prevent tempera-

ture gradients in the liquid phase. In this case the crystallization starts in the coldest place, and the subsequent crystal growth proceeds in accord with the temperature distribution. Thus, for example, in the presence of a heat lead in the ampoule shown in Fig. 2h, the formation of a transparent solid phase begins on the surface of the heat lead, and the interface boundary duplicates exactly the contours of this lead. Further growth of the crystal is accompanied by leveling-off of the surface in accord with the shapes of the isotherms on the interphase surface. As shown by further experiments, a sample can be grown in similar manner also from the superfluid liquid phase. In this case, however, the crystallization should proceed extremely slowly and in the presence of a directed heat flux that produces a preferred direction in the crystallizer volume.

The described experiments have thus been able to establish the principal qualitative features of helium-crystal growth. As a result, Shal'nikov [10] developed a technique for growing single-crystal samples with provision, besides visual observations, for continuous temperature monitoring and control of the growth process. When high-grade single crystals are grown it is obviously necessary to carry out the crystallizations under conditions as close as possible to equilibrium, i.e., at constant pressure and temperature. This is hindered, however, by the following circumstance. Solidification sets in at the coldest place, in which case the latent heat released during the crystal growth is automatically removed through the produced solid helium whose thermal conductivity on the melting curve is quite low and does not exceed 10^{-2} W/cm \cdot K. As a result, a temperature gradient is inevitably produced in the growing crystal and is larger the higher the growth rate. Thus, in the temperature region above 1 K, where the heat of crystallization differs substantially from zero, the only real process in which crystal growth takes place under conditions closest to equilibrium is crystallization at a constant pressure in a specified temperature gradient.

Shal'nikov [10] used a standard He^3 refrigerator placed inside glass helium and nitrogen Dewar vessels. Figure 4 shows schematically the glass vacuum chamber of the refrigerator, in which the glass ampoule for the crystal growth is located. Sealed into the lower part of the ampoule is a copper heat lead that is in thermal contact with the bath of the He^3 refrigerator. Fused into the upper cover of the ampoule is a capillary that connects it with the high-pressure system. The vacuum

*We have in mind here the pressure measured at the entry into the capillary at room temperature. The difference between this and the equilibrium pressure corresponding to the melting point determines the rate of flow in the capillary, and therefore the crystallization rate.

**We recall that we are dealing here with temperatures above 1.2 K.

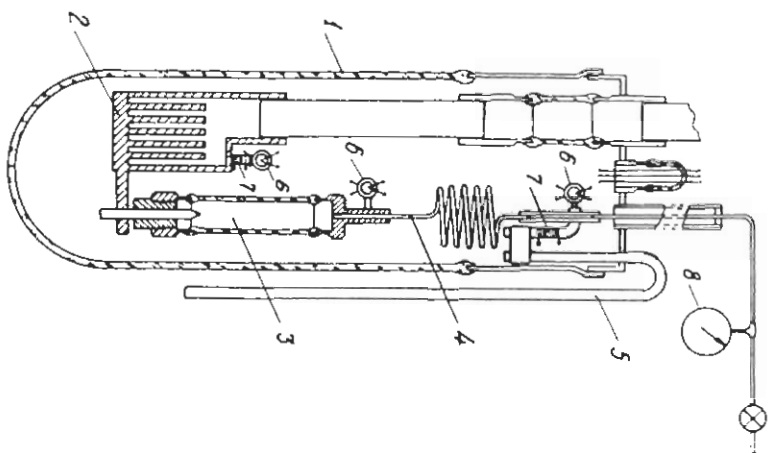


Figure 4 Diagram of low-temperature part of helium crystal growth apparatus [10]. 1—Glass vacuum jacket, 2—He³ bath of refrigerator, 3—ampoule, 4—high-pressure capillary, 5—heat lead, 6—thermometers, 7—heaters, 8—manometer.

insulation of the high-pressure line inside the cryostat, provided in the construction, made blocking of the working volume impossible. To cool the helium flowing into the ampoule, a segment of the capillary inside the vacuum chamber is connected with the heat lead that provides the thermal contact with the external helium bath. Mounted on the heat lead are a thermometer and heater intended to monitor and regulate the capillary temperature. In the upper and lower parts of the ampoule are placed two thermometers that record the temperature distribution during the crystal growth. This distribution could be regulated with a heater mounted on the cover of the ampoule.

Before the start of the crystallization, the entire cryostat was cooled to a temperature somewhat higher than the suggested solidification temperature, and the desired pressure was established in the ampoule. The ampoule and the manometer (the latter at room temperature) were disconnected from the remaining parts of the high-pressure system and the slow cooling was started. When the solidification temperature was reached, a transparent layer of solid helium was produced on the heat lead. The subsequent cooling was accompanied by upward motion of the interphase surface, which leveled-off with increasing distance from the heat lead and became horizontal. By regulating the cooling rate and using the heater in the upper part of the ampoule, it was possible to carry out the crystallization at a specified rate, which could be varied in a wide range. From measurements of the temperatures of the upper and lower ends of the ampoule and of the position of the interphase surface it was easy to determine (in the linear approximation) the temperature distributions in solid and liquid phases. As a rule, the crystal growth rate did not exceed 1–3 cm/hr, in which case the characteristic values of the temperature gradients amounted to 0.1–1 K/cm. During the crystallization time, the temperature of the cooled section of the capillary was continuously monitored and maintained above the solidification temperature with the aid of the heater. Since the volume of the ampoule was small compared with volume of the manometer, the crystal growth took place at almost constant pressure. After the end of the crystallization, the heating of the capillary was stopped and the capillary was filled with the solid phase. All the subsequent temperature measurements were therefore made at a fixed volume.

The procedure considered for growing crystals at constant pressure made it possible to obtain samples of exceptionally high quality. By using this method, Mezhev–Deglin succeeded in growing crystals whose thermal conductivity reached the record value 50 W/cm²·K, and in which the mean free path of the phonons exceeded the sample diameter by several times [11]. Crystal growing at constant pressure has found extensive use during the last decade. At the same time, a need arose for effective methods of controlling the quality and the orientation of the samples. The most direct and informative among these methods are x-ray structure analysis [12–14] and neutron diffraction [15]. The capabilities of the x-ray structure method were first demonstrated by Fain and Lazarus [12] in measurements of the

thermal conductivity of He^4 . Somewhat later Graywall [13], while investigating the anisotropy of the sound velocity of hcp He^4 and bcc He^3 , investigated in detail the influence of the growth conditions on the quality of the crystals. Most crystals grown by the constant pressure at a rate ~ 1 cm/hr, despite the small changes of the pressure in the course of the crystallization, were shown by the x-ray diffraction pattern to be of high grade, to contain no stresses, and to require no annealing. At the same time, all attempts to grow a good crystal from superfluid helium by slow compression of the liquid at constant temperature ended in failure.

Some of the crystals grown at constant pressure were defective in structure, and a correlation was observed between the growth rate and the number of defects in the sample. It must also be noted that, regardless of their quality, all the samples, including even the polycrystalline ones, had absolute optical transparency.

An optical control method, based on birefringence, has lately come into extensive use. This method yields extensive, albeit not complete, information on the orientation and on the quality of the crystals. It can be used, however, only for the investigation of hcp He^4 [16-19].

Intensive research into such structure-sensitive properties as the thermal conductivity [19,20] and the propagation and attenuation of sound [13,17,19] has made possible the use of these properties to determine the orientation and the degree of perfection of the crystals.

When speaking of the study of solid helium as a whole, it must be noted that up to very recently the researchers focused on the study of bulk properties, while the investigation of the surfaces of helium crystal was set aside. For this reason, apparently, practically no investigations were made of a narrow phase-diagram region located along the melting curve below 1.2 K. At higher temperatures, the kinetics and shapes of the growth observed in the course of the crystallization led only to rather indirect conclusions concerning the state of the crystal surface. The absence of faceting and of supercooling at high growth rate pointed to an atomically rough structure of the helium surface at high temperature [5,14]. As already noted in the preceding section, at sufficiently low temperatures the classical equilibrium surface is atomically smooth. However, taking the role of the quantum effects into account, Andreev and Parshin [5] predicted the existence of a qualitatively new surface state, which is the analog of

an atomically rough surface and is at equilibrium down to zero temperature. The most significant result of the theory was the predicted possibility of nondissipative crystallization and of the existence of crystallization waves.

Up to that time, the only experimental indication of the unusual properties of the surface of solid helium were the observations of Shal'nikov and co-workers [21], who investigated the hardness of crystalline helium. The most interesting result of these experiments was the anomalously rapid refilling of an indentation produced on the crystal surface by an applied force. The crystallization rate reached in this case $100 \mu\text{m}/\text{sec}$ and could not be attributed to any temperature effects whatever.

III Features of He^4 Crystal Growth at Temperatures

Below 1.2 K

Our latest experiments [6,7] were entirely devoted to the investigation of the surfaces of He^4 crystals at temperatures below 1.2 K. The optical instrument was designed to ensure prolonged continuous operation and made it possible to observe the crystal growth, to take photographs, and to perform optical measurements. In the lower part of the metallic cryostat, provision was made for three pairs of plane-parallel windows (K-8 glass at room temperature, single-crystal sapphire at nitrogen temperature, and chemical glass at helium temperature). The windows in the vacuum jacket of the He^3 refrigerator were made of fused quartz. In all other respects, the construction of the apparatus duplicates that shown in Fig. 4.

The He^4 crystals were grown in a metallic ferrochrome chamber of rectangular 12×15 mm cross section (Fig. 5). Two opposite walls, made of chemical glass measuring $12 \times 28 \times 3$ mm were left open to permit observation of the entire volume of the container. The glass was sealed into the metallic housing with Sycast-1266 epoxy resin. When constructed with precision (the gap between the glass and the metal did not exceed $50 \mu\text{m}$ over the entire perimeter), such a construction could withstand repeated cooling from room temperature to helium temperature and a pressure up to 60 atm. A capacitor intended for the excitation of the crystal surface oscillations was

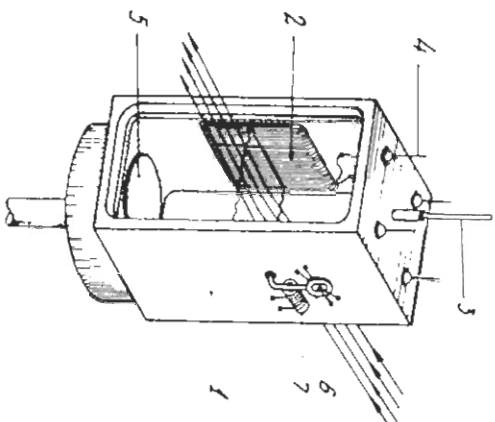


Figure 5. Construction of crystal-growth chamber [6, 7]: 1—housing; 2—capacitor; 3—capillary; 4—electric lead-in; 5—heat lead; 6—thermometer; 7—cadmium reference. The arrows indicate the direction of the light beam.

mounted on a side wall inside the chamber. The capacitor consisted of two capron (nylon)-insulated copper wires of 30 μm diameter, bifilarly wound (150 turns) on a Fiberglass plate; it withstood in liquid helium a voltage not less than 3 kV, corresponding to a maximum field intensity $(2-3) \cdot 10^6$ V/cm. In the upper part of the chamber were sealed-in a capillary and the electric leads, while in the lower, the copper heat lead to the He^3 bath. To decrease the heat flow into the chamber, part of the capillary was in thermal contact with the He^3 bath. A carbon thermometer mounted on a heat lead sealed into the side wall of the chamber was calibrated against the He^3 vapor pressure. The calibration was monitored with a cadmium reference ($T_c = 0.515$ K), mounted on the same heat lead. When the chamber was filled with superfluid helium, the total heat inflow into the He^3 bath, including that by radiation through the windows, did not exceed 10^{-4} W.

The crystals were grown from He^4 subjected to preliminary purification with the aid of the thermochemical effect. Thus, the He^3 concentration in the initial gas did not exceed 10^{-8} . Since the slope of the melting curve at temperature below 1.2 K is practically zero, the

method described above for growing crystals at constant pressure cannot be used in this region of the phase diagram. The crystals were grown by slow compression of the liquid at constant temperature, and the rate of crystallization was determined by a controlled flow of helium inside the chamber. The chamber was first filled with liquid helium at approximate pressure 25 atm with the aid of a compressor, which was subsequently disconnected. The growth and melting of the crystals was effected by heating and cooling the outer ballast volume (300 cm^3). When necessary, the grown crystal could be completely melted within less than a minute, by simply lowering the pressure in the buffer volume by 0.1–0.2 atm below the melting curve. The growth process could then be repeated at any desired velocity. Continuous visual control made it possible not only to repeat the crystallization many times during one experiment, but also to partially melt and grow crystals, to leave in the chamber a seed measuring 1 mm^3 for subsequent growth of a large crystal, etc. Once the necessary sample was grown, the buffer volume was disconnected and the position of the interphase boundary could remain unchanged accurately to 0.1–0.2 mm for many hours.

Visual observation of the crystallization of He^4 reveals a great variety of shapes and growth dynamics, depending on the temperature, on the place of nucleation, and on the orientation of the nucleus. At temperatures below 1.2 K, the crystallization proceeds as a rule from a single center randomly located on one of the chamber walls. In the course of the growth, the crystal is always faceted to one degree or another, with the faceting more pronounced the faster the growth and the lower the temperature. The observed faceting always corresponds to a hexagonal prism represented by some faces or others, depending on the point of nucleation, the size of the crystal, and its orientation relative to the chamber wall (Fig. 6). The crystal symmetry (hexagonal close packed, space group $D_{6h}^{4,4}$) makes it possible to identify the basis of the prism with the (0001) basal plane, and the lateral faces perpendicular to it with planes of the type $\{10\bar{1}0\}$, or $\{11\bar{2}0\}$. Thus, direct observation of the crystal during the growth makes it possible in essence to establish uniquely its orientation. Figure 6 shows clearly all the characteristic features of the growth of the He^4 crystals at low temperatures: a distinctly pronounced faceting at relatively high growth rate—0.1 mm/sec and higher (frames a and b), the rounding-off in the upper part of the surface as the growth

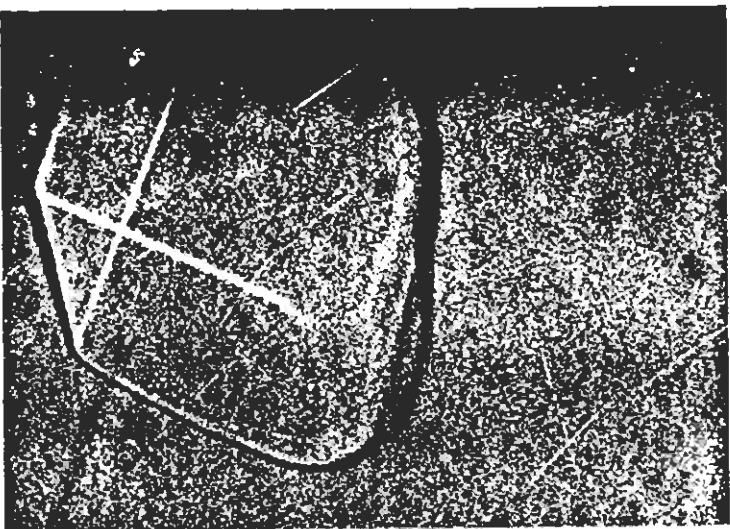


Figure 7. Crystal under conditions close to equilibrium at a temperature 0.5 K. The lower face is represented by the (0001) plane; the crystallization wave due to the vibrations of the crystal can be seen on the upper rounded surface.

helium from all other crystals and cannot be explained within the framework of the classical theory.

The crystallization and melting processes proceed at a noticeable rate even at a fixed amount of helium inside the chamber (when there is no flux of matter through the filling capillary) under the action of the most insignificant moving forces, such as surface tension or gravity. This is manifested most clearly in the case when a small sample is grown on one of the side walls of the chamber, so that the crystal is surrounded by the liquid phase from all sides; with the exception of the plane of the contact with the wall (Fig. 7). Under the influence of gravity the crystal, gliding as it were down the wall, moves slowly downward. What actually occurs is a recrystallization of

the sample, as is evidenced by its shape. The upper rounded-off part of the crystal is continuously melted, whereas the lower faceted part grows. We emphasize that this process takes place under the action of the hydrostatic pressure difference, at a vertical crystal dimension 5-6 mm, at a rate of ~ 1 mm/min. At a definite sample orientation, when the lower part of its surface is mainly the (0001) face, the recrystallization is exceedingly slow, so that the crystal can hang on the chamber wall for several hours.

During the growth time, a phenomenon which we call crystal "dumping" is frequently observed. The cause of the dumping is usually some obstacle encountered in the path of the growing crystal. This may be a roughness on the substrate surface, the opposite wall or the bottom of the chamber, which limit further growth of the crystal. In this case a rapid (less than 0.1 sec) avalanche-like recrystallization of the sample takes place, appearing outwardly as if the crystal were to collapse and fill partially or completely the lower part of the chamber (Fig. 8). The faceting, which does not exist in the course of the dumping, is then immediately restored and uniform growth of the crystal continues. Even though the dumping changes considerably the shape of the crystal, its orientation is fully preserved. In most cases this process is accompanied by the appearance of one or several planar defects, apparently the stacking faults* well investigated in ordinary close-packed structures. At equilibrium, these faults appear in the form of "ravines," which are produced at the places where the defect plane emerges to the surface of the crystal (Fig. 9a). The occurrence of the ravines is obviously due to the excess fault energy, which is proportional to its area. The observed ravine depth makes it possible to estimate this energy at 0.1-0.2 erg/cm². It must be emphasized that the orientations of the blocks on both sides of the stacking-fault plane are strictly identical. When the growth of a crystal with such faults resumes, the ravines are rapidly grown over, and the resultant faceting does not differ in any way from that of a fault-free crystal (Fig. 9b). The last circumstance is the principal

* It is known that the difference between two possible close-packed structures can be easily traced with close packing of hard spheres as the example. The alternation of the layers for a fcc structure corresponds to the sequence ABCABC..., whereas for the hcp structure it is ABAB.... In this notation, the stacking fault can be represented by sequences of the type ABABCACA...., ABABCBCB...., and possibly also by more complicated ones.

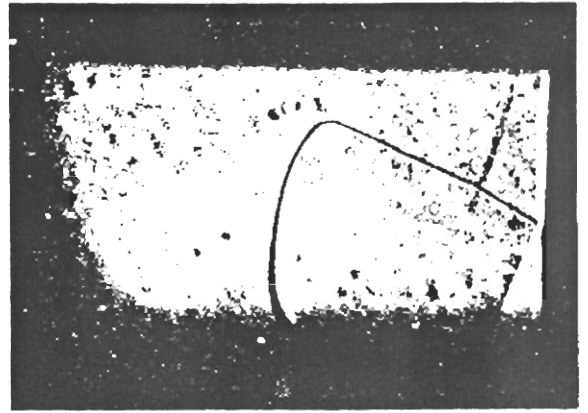
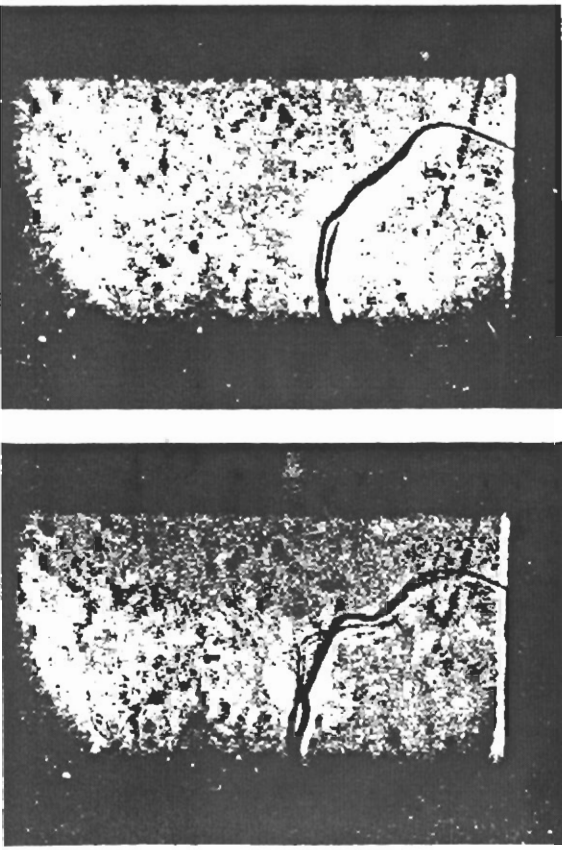
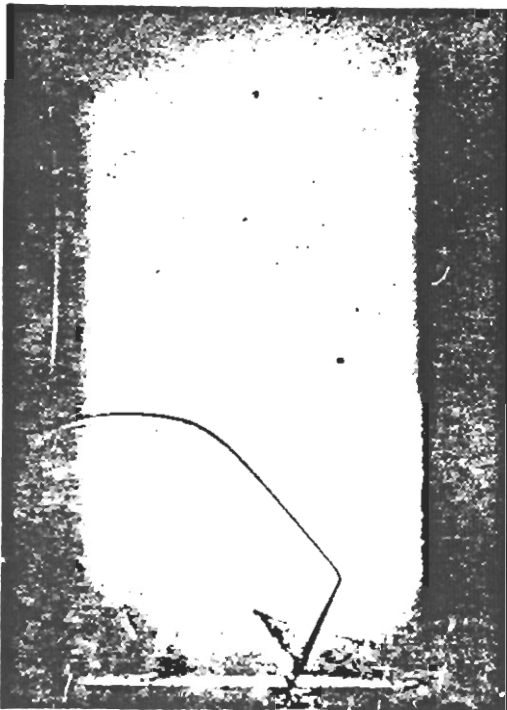
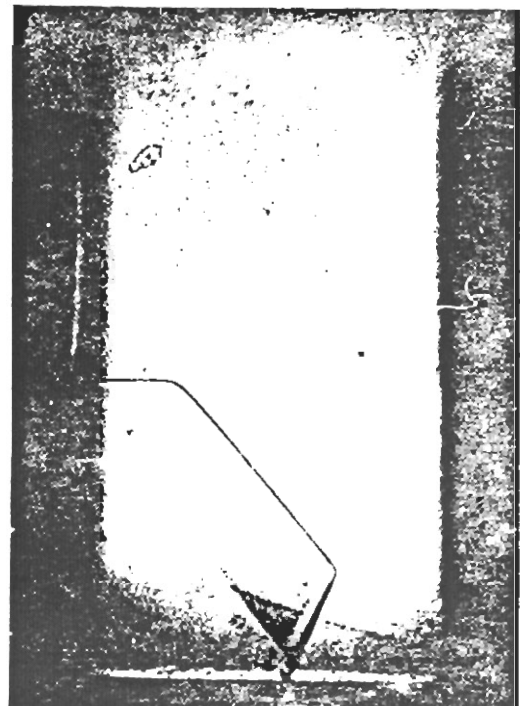


Figure 8 Motion pictures of crystal "dumping," taken at 24 frames/sec.



a



b

Figure 9 External view of crystal with defect: a) at equilibrium; b) during growth.

difference between the stacking fault and other types of two-dimensional crystal defects. Thus, e.g. in the presence of two disoriented blocks at the places where the block boundary emerges to the sample surface, characteristic peculiarities of the same plot are observed both at equilibrium and during the growth time.

Stacking faults are apparently the most frequently encountered disturbance to the structure of crystals grown at temperature below 0.8 K, since it is quite complicated to avoid dumping and to grow a sufficiently large fault-free sample. However, neither x-ray structure analysis nor any of the methods considered above is suitable for the detection of a stacking fault, which has such a distinct structure. The only method of determining the crystal quality in this case is apparently visual monitoring of the equilibrium shape of the surface. Experience has shown that the most favorable regime for the production of a fault-free sample of large size is slow crystallization at a temperature 0.8–1.0 K. At these temperatures, the anisotropy of the growth coefficient is still not so large and, in addition, the anomalously high crystallization rate which contributes to the appearance of dumping is absent.

When speaking of crystal quality, it must be borne in mind that when a sample grown, say, at 0.8 K is heated to 1.1 K and above, an irreversible change takes place as a rule in the shape of its surface. This change is probably due to plastic deformation of the crystal as a result of a change in equilibrium pressure by an amount ~ 0.1 atm, which exceeds the yield strength of solid helium [21,24]. Only a sufficiently slow (not faster than 0.1 K/hr) temperature change is not accompanied apparently by plastic deformation of the crystal.

As already noted, solidification at low temperatures takes place usually on account of the growth of one crystal. However, by applying to a capacitor a voltage of ~ 1 kV we succeeded in initiating the growth of one or several more crystals on the surface of the capacitor in the presence of a large sample filling the entire lower part of the chamber. After the dimensions of the crystal grown on the capacitor reached 3–4 mm, the electric field was turned off and the crystal dropped under the influence of gravity. Thus, it becomes possible to observe the growing-together of two blocks having different orientations. Outwardly, this process has the appearance of the coalescence of two liquid drops. When the contact takes place, the upper crystal decreases rapidly inside and vanishes, ensuring thereby the additional

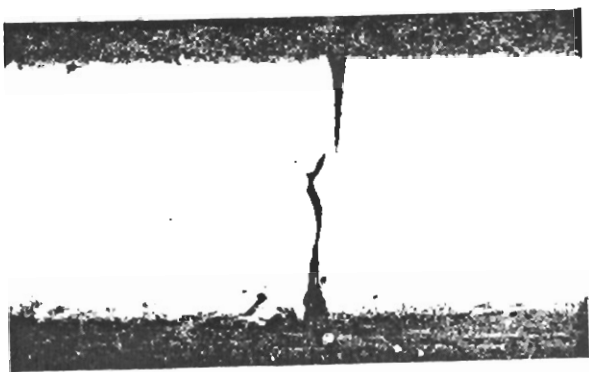


Figure 10 Shape of the surface of a crystal with a block structure.

growth of the lower crystal, which takes place without any noticeable violation in the structure of the latter. The process considered is possibly one of the reasons why, as noted by various authors, it is difficult to grow a block crystal at low temperatures. The foregoing does not mean, however, that a block crystal cannot exist at such temperatures. On the contrary, a crystal grown at a temperature higher than 1.3 K from several nuclei retains its block structure when cooled down to the lowest temperatures (Fig. 10).

Notice should be taken of an interesting phenomenon that can be observed by applying to a capacitor, frozen into the solid phase, a sufficiently high (~ 1 kV) alternating voltage. Under these conditions, bubbles are produced on the surface of the capacitor in the crystal below the principal meniscus; these bubbles are obviously filled with liquid helium, and reach sizes of several millimeters (Fig. 11). The bubbles have a clearly pronounced faceting, and all the bubbles have the same orientation as the crystal. They are very mobile, they are produced and vanish rapidly, moving upward over the surface of the capacitor, etc. Those of them that are particularly large can some-

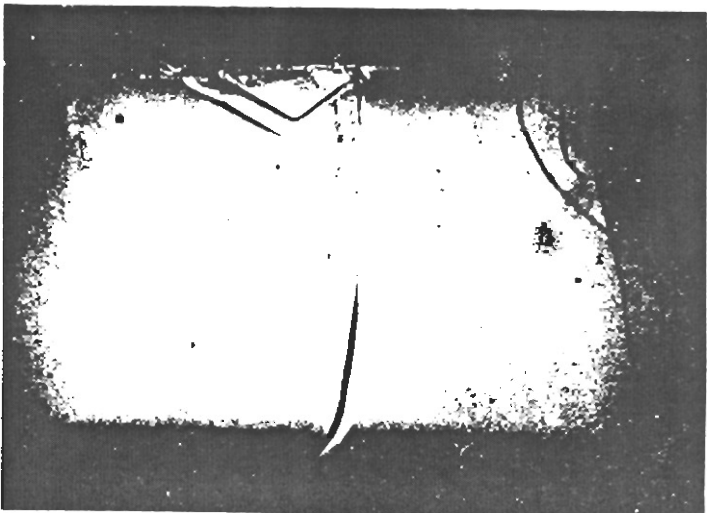


Figure 11. Appearance of bubbles in an electric field. The upper half of the chamber is filled with liquid helium and the lower with the crystal; two faceted bubbles can be seen on the left below the meniscus on the capacitor.

times break up, so that one or several bubbles turn out to be frozen inside the volume of the crystal: such bubbles lose their mobility practically completely.

Of great practical importance is the question of the place of production of the nuclei and of their orientation. We note first that the nuclei are never produced directly in the volume of the liquid. This is perfectly natural, since superfluid is a much purer object than the inner walls of the chamber, where there are always enough crystallization centers. Furthermore, in our experiments, as in most other experiments with helium crystals, the inner walls of the chamber have a rather complicated geometry and are made of a great variety of materials (ferrochrome, copper, glass, Fiberglas plastic, capron,

adhesives). In addition, no special measures were made to finish and clean these surfaces thoroughly. Under these conditions, one can hardly expect any regularities with respect to the point of nucleation and orientation of the nuclei of helium crystals. Indeed, the nucleus usually appears at some random point of the surface, and the point of its appearance can vary, e.g., when the chamber illumination conditions are changed. As for the orientation of the nuclei, there is observed here (see also [34]) the unique phenomenon of "orientation memory," which seems rather puzzling to us and consists in the following. When the crystal growth process in a single experiment is repeated a number of times, wherein the grown crystal is melted, the pressure is lowered by 0.1–1 atm below the melting curve, and then again rises until a new nucleus is produced, the latter has as a rule the same or nearly the same orientation as its predecessor. This repetition of the orientation takes even in those cases when the new nucleus is produced in an entirely different place in the chamber than the preceding one (we emphasize that in all this time we are speaking visible nuclei, i.e., of crystals with dimension of the order of 1 mm). This "memory" can be destroyed by a sufficiently strong change of the conditions in the chamber: thus, according to [34], it suffices for this purpose to decrease for a while the pressure by several atmospheres. In our apparatus it is possible to control partially the orientational memory by applying to the capacitor a sufficiently high voltage (~ 1 kV). When the electric field is turned on, the nucleus is produced directly on the surface of the capacitor and has already a new orientation, which is in fact "remembered" by the succeeding nuclei. We note once more that this phenomenon is quite puzzling: at any rate, mere reference to a van der Waals force at the wall, as in [34], casts no light whatever on the question.

IV Surface Structure and Growth Kinetics of Quantum Crystals

The described picture of the helium crystal growth means that at all orientations, with the exception of the special ones determined by the faces of the growth prism, the crystal surface remains in an atomically-rough state at least down to 0.4 K. The fact that the growth

coefficient for these orientations increases rapidly with decreasing temperature suggests that this state differs in its properties from the usual atomically rough state. It will be shown below, by taking quantum effects into account, that the surface of a helium crystal, at sufficiently low temperatures, can indeed be in a special state that is the quantum analog of a classical atomically rough surface.

When it comes to a microscopic description of the structure of a crystal-liquid interphase surface difficulties arise even in the classical theory. The reason is that a unique classification of each particle of the substance as belonging to one phase or another is generally speaking impossible because of the complicated character of the particle motion near the interphase surface. Particles belonging to different phases can be distinguished satisfactorily only for an atomically smooth surface that contains no mobile defects. In the case of the boundary between a quantum liquid and a quantum crystal, the need for explicitly taking into account the fact that identical particles are quantum-mechanically indistinguishable makes their individualization impossible regardless of the surface structure. In a microscopic description of the structure of the surface it would be necessary in this case to use a density function that is periodic in the bulk of the crystal and equal to a certain constant in the bulk of the liquid. The width of the transition region between these two asymptotic limits, which has the meaning of the effective thickness of the boundary, will be in this case of the order of several interatomic distances.

It is essential, however, that such concepts as a step or a kink on a step, which have symmetry implications, can be introduced also in the quantum case. It suffices for this purpose to use only the general properties of the boundary that follow from the symmetry of the phases in contact. For example, a step on a surface corresponds to such a state of the boundary wherein its position at infinity (on the right and on the left in Fig. 12) is shifted by an elementary crystal translation vector that does not lie in the plane of the surface. By virtue of the periodicity of the crystal and of the homogeneity of the liquid, a shift equal to the translation vector transfers the boundary to an equivalent position, so that the step constitutes a certain linear defect on the surface and, in essence, only this surface property is important in what follows. We emphasize that in this way it is possible to introduce the concept of a step, and analogously the

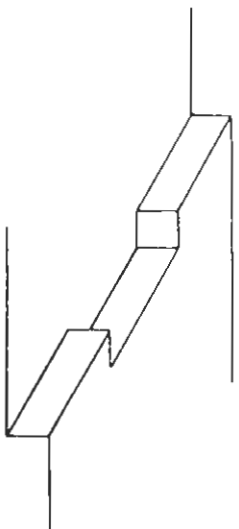


Figure 12 Step with two kinks.

concept of a kink on a step on a surface having arbitrary integer Miller indices.

The state of the step is determined by the configuration of the kinks on it, and the kinks can be of two "signs" (see Fig. 12). Each kink can be regarded as a point defect on a step. Assume that some definitely oriented step with a kink is present on the surface in the equilibrium state at $T = 0$. Displacement of the kink by the translation elementary vector along the step corresponds to a transition of one particle (the helium atom) from one phase to another. Such transitions take place with finite probability even at $T = 0$, on account of processes as similar to quantum below-barrier tunneling. The kink energy is not altered by such displacements, since the chemical potentials of the phases in equilibrium are equal. This means that in analogy with other point defects in a quantum crystal, the kink behaves under these conditions as a delocalized quasiparticle whose state is determined by the quasimomentum.

The kink energy ϵ is a certain function of its quasimomentum p (see Fig. 13), with the width of the energy band Δ proportional to the probability of tunneling of one atom per unit time: $\Delta \sim h\nu$. In this case this probability is apparently not less than the corresponding

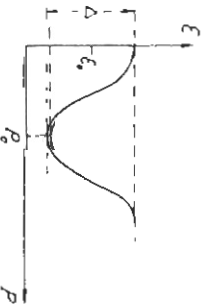


Figure 13 Energy spectrum $\epsilon(p)$ of solitary kink.

probability that determines the width of the vacancy band in He^4 . Thus, one should expect in our case Δ to be of the order of 1 K.

Let p_0 be the value of the quasimomentum corresponding to the bottom of the energy band. At $T = 0$ this state is stationary (and ground) for a solitary kink. Stationary states that are close in energy ($p \rightarrow p_0$) correspond to nonzero kink velocities, and therefore to a continuous flux of matter from one phase to another. In other words, the transition of matter from one phase to another is in this case a coherent process unconnected with any energy dissipation whatever. In fact, loss of coherence could occur here only as a result of collisions between the kink and the phonons or their radiation. At $T = 0$, however, there are no thermal excitations, and the phonon radiation at low kink velocities are forbidden by the energy and momentum conservation laws. We emphasize also that the considered states are not separated from the ground state by a finite energy gap. Thus, a solitary kink is an example of a system having stationary states that are arbitrarily close in energy to the ground state and are characterized by the presence of continuous flux of matter from one phase to another.

Just for any classical defect, energy ϵ_0 of a localized kink is a positive quantity. On the other hand, a localized kink constitutes a "packet" made up of states will all possible values of p . Therefore ϵ_0 lies approximately near the midpoint of the energy band. If the energy $\epsilon(p_0)$ corresponding to the bottom of the band is positive, then there are no kinks in the ground state of the step, i.e., the step is atomically smooth at $T = 0$. On the other hand if Δ is large enough (roughly speaking, $\Delta > 2\epsilon_0$), then $\epsilon(p_0) < 0$, i.e., when kinks with $p = p_0$ appear, the energy of the step decreases. In other words, the atomically smooth state turns out in this case to be unstable with respect to production of kinks (more accurately speaking, of pairs of kinks of opposite sign, inasmuch as at a fixed average orientation of the step the production of kinks of only one sign is impossible). To clarify the structure of the ground state of the step in this case it is necessary to take into account the interaction between the kinks.

When two kinks of the same sign collide, they can exchange quasimomenta (Fig. 14a). On the other hand, if the signs of the kinks are opposite, then, besides collisions of the same type, a process with "flip-over" into a neighboring row is also possible (see Fig. 14b), and the probability of this process is by far not small. In fact, at distances

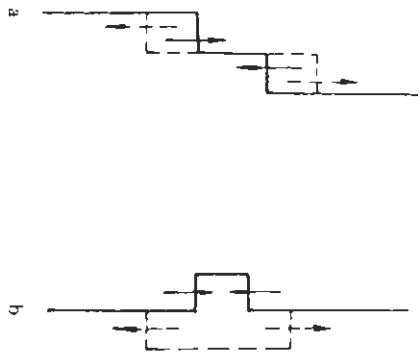


Figure 14 Possible types of kink collisions.

that are large compared with atomic, the interaction of the kinks is due mainly to their interaction via the field of the elastic strains in the crystal [25]. In this case

$$U_{in}(r) \sim \frac{\epsilon_0^2}{E} \frac{1}{r^3} \quad (a)$$

where E is Young's modulus (the van der Waals interaction yields $U_{in} \sim r^{-4}$). On the other hand, at distances of the order of atomic, obviously, $U_{in} \sim \epsilon_0$. The probability of the process with "flip-over" is the probability of particle tunneling through the potential barrier determined by the function $U_{in}(r)$, and can reach values of the order of unity under the conditions considered. Next, it is clear that if the energy $\epsilon(p_0)$ is not too close to zero ($|\epsilon(p_0)| \sim \Delta/2$), then the interaction between the kinks is substantial only over distances of the order of atomic.

Thus, when the concentration of the kinks on the step is increased, its energy decreases until it reaches a minimum at a certain concentration (generally speaking, on the order of atomic). Such a step can be called "quantum-rough," since it contains a large number of kinks even in the ground state. A substantial property of such a step is the presence of states that are arbitrarily close in energy to the ground state and correspond to continuous motion of the step, accompanied by particle transitions between the phases. The presence of such states

is ensured by the "flip-over" into the neighboring row, which was considered above. A quantum-rough step turns out thus to be completely delocalized on the crystal surface.

The total energy β of a quantum-rough step (referred to the length of the elementary translation vector along the step) may turn out to be positive as well as negative, depending on whether the positive "bare" energy β_0 of the atomically smooth step compensates for the negative energy of the delocalized kinks with account taken of their interaction. If $\beta > 0$ for all the possible orientations of the step on the considered surface, then there are no steps in the ground state of the surface, and at $T = 0$ the surface remains in the classical atomically smooth state. If however $\beta < 0$ for at least one pair of opposite orientations of the step (of course, more complicated configurations are also possible), then the atomically smooth surface turns out to be unstable to the production of such steps. As a result, the equilibrium surface constitutes a distinctive two-dimensional liquid consisting of delocalized steps of various configurations, including closed steps of finite length. The number of steps of each kind is obviously not fixed and is itself determined from the condition that the total energy be a minimum.

Crystal growth with such a surface is due both to an increase of the surface bounded by each step, and to the formation of new atomic layers when two steps collide (this process is analogous to the flip-over to the neighboring row when two kinks collide). It is important that these processes and their inverses produce in the system stationary states that are arbitrarily close to the ground state, and in which a continuous growth and melting of the crystal takes place. The motion of the interphase boundary at $T = 0$ takes place thus without loss of phase equilibrium. In other words, the kinetic growth coefficient for a crystal with such a surface at zero temperatures becomes infinite.

As for a crystal with an atomically smooth surface, the situation here is reversed. In fact, at equilibrium at $T = 0$, the atomically smooth surface does not contain any defects whatever. Therefore a crystal with such a surface can grow only by formation of nuclei of new atomic layers, i.e., closed steps of finite length, whose energy according to the foregoing is in this case positive. If a finite chemical-potential difference $\Delta\mu$ exists between the phases, then the formation of a nucleus of critical dimension by quantum tunneling becomes possible [26]. As $\Delta\mu \rightarrow 0$, the critical dimension increases without

limit, the probability of this process tends rapidly (exponentially) to zero, so that $K = \lim_{\Delta\mu \rightarrow 0} (V/\Delta\mu) = 0$. Thus, the kinetic growth coefficient of a crystal with atomically smooth surface is zero at $T = 0$.

We see thus that at absolute zero the kinetic growth coefficient is either zero or infinite, depending on whether the crystal surface is in an atomically smooth or a quantum-rough state. Of course, one crystal can have surfaces of both types, depending on their orientation. In the case of He^4 hcp crystals, as shown by the experimental data [23, 7] surfaces of only two orientations, corresponding to the prism-growth faces, remain in the atomically smooth state, while the surfaces of all the remaining orientations turn out to be in the quantum-rough state. This fact is perfectly natural, since it is precisely the indicated special orientations that correspond to the closest packed faces, for which maximum values of β_0 should be expected. A question that remains open, however, is which of the possible orientations, $\{10\bar{1}0\}$ or $\{11\bar{2}0\}$, correspond to the lateral faces of the growth prism and whether the difference between these orientations, in the sense discussed above, is purely quantitative or has some hidden more interesting cause.

At finite temperatures, the growth of a crystal with a quantum-rough surface is accompanied by energy dissipation due to the interaction of the bulk thermal excitations with the moving surface [5]. Let us consider, e.g., the dissipation due to phonons. Phonons incident on the boundary from the liquid side, produce a pressure $P_{ph} \sim \epsilon_{ph} \sim nT^4\Theta^{-3}$ (n is the number of atoms per unit volume and Θ is the Debye temperature). At equilibrium, i.e., when the boundary is immobile, this pressure is offset by the counterpressure of the solid. If the boundary moves with velocity V , then, as a result of the Doppler effect, a pressure difference $\Delta P_{ph} \sim (V/c)\epsilon_{ph}$ (c is the sound velocity) is produced on the boundary and is directed opposite to the motion. As a result, an energy of the order of $(V^2/c^2)\epsilon_{ph}$ is dissipated per unit surface area. On the other hand, the same energy dissipation is equal to $\Delta\mu N$, where $N = nV$ is the number of atoms that go over per unit time from one phase to the other. From this we get

$$K \sim c \frac{\Theta^3}{T^4} \quad (3)$$

Thus, the growth coefficient becomes infinite at $T \rightarrow 0$ in proportion to T^{-4} .

Phonons are the main type of thermal excitations in liquid He⁴ at temperatures lower than approximately 0.5 K. At higher temperatures, a more substantial role may be played by the contribution of the rotons to the total energy dissipation. In this case one should expect a relation $K \sim \exp(\Delta/T)$, where Δ , is the roton gap.

Everything said above pertained so far to He⁴ crystals. As for He³ crystals, an equation similar to (3) can be used for them only at extremely low temperatures, much lower than the superfluid-transition temperature (and, of course, under the condition that the crystal surface remain in the quantum-rough state). In this case, however, the main type of thermal excitations, in both the liquid and solid phase, are spin waves with a dispersion law that is linear, just as for the phonons [27]. The main contribution to the energy dissipation is made here by the spin waves of the crystal, since their velocity is lower. Therefore the quantity c in Eq. (3) has in this case the meaning of the spin-wave velocity in antiferromagnetic solid He³, while Θ has the meaning of the Néel temperature. At higher temperatures, in which liquid He³ behaves like a normal Fermi liquid, the principal dissipation mechanism is the interaction of the moving boundary with the Fermi excitations. The order of magnitude of the energy dissipation is $p_F \cdot nV \cdot V$, where p_F is the Fermi momentum; this corresponds to a temperature-independent growth coefficient $K \sim 1/p_F$. A similar estimate can be obtained also for the case of a solution of He³ in He⁴, with a concentration $n_3/n_4 \ll 1$. In this case, the energy dissipation due to the interaction of the moving boundary with the impurity particles is of the order of $n_3 p_3 V^2$, corresponding to a growth coefficient $K \sim (n_3/n_4)(1/p_3) p_3$ is the characteristic momentum of the impurity). Comparing with Eq. (3), we see that at low temperature the He³ impurity can substantially influence the growth kinetics of He⁴ crystals even at quite small concentrations.

V Equilibrium Shape of Helium Crystals

The equilibrium shape of any crystal is determined by the condition that its surface energy $\alpha(\varphi_1, \varphi_2)$ be a minimum at a fixed volume:

$$\oint \alpha dS = \min \tag{4}$$

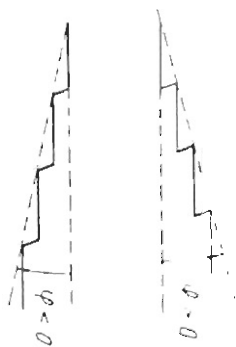


Figure 15 Stepped faces (illustrating the derivation of the discontinuity $\Delta(\alpha/\lambda\varphi)$)

The solution of this variational problem is given by the Wulff theorem, which makes it possible to construct in explicit form the equilibrium shape of a crystal from the known function α .

As shown by Landau [28], the presence of faceting, i.e., of flat sections in the equilibrium shape of the crystal, is due to the specific properties of the function $\alpha(\varphi_1, \varphi_2)$, which are caused in final analysis by the discrete character of the crystal lattice. Namely, for a flat surface section with a given orientation to appear, it is necessary that the derivative $\partial\alpha/\partial\varphi$ for this orientation experience a finite discontinuity. At $T = 0$ in a classical crystal, this property is possessed by the surface of arbitrary integer Miller indices. In fact, let us consider one such face (Fig. 15). Let α_0 be the surface energy for this face. Faces with orientations close to the initial one, i.e., inclined to it by a small angle φ , can be regarded as steplike. At $T = 0$, a classical step has a certain positive energy proportional to its length (β_1 and β_2 for "positive" ($\varphi > 0$) and "negative" ($\varphi < 0$) steps, respectively). At $\varphi \ll 1$ the distance between steps is large and their interaction can be neglected. The surface energy $\alpha(\varphi)$ of an inclined face is consequently equal to the sum of α_0 and of the energy of the steps per unit area:

$$\alpha(\varphi) = \begin{cases} \alpha_0 + \frac{\beta_1}{a} \varphi, & \varphi > 0 \\ \alpha_0 - \frac{\beta_2}{a} \varphi, & \varphi < 0 \end{cases} \tag{5}$$

(a is the height of the step), from which it is seen that the derivative $\partial\alpha/\partial\varphi$ has at $\varphi = 0$ a finite discontinuity $\Delta(\partial\alpha/\partial\varphi) = (\beta_1 + \beta_2)/a$. According to Landau [28], the solution of the variational problem (4) does indeed lead in this case to the conclusion that a flat surface section with $\varphi = 0$ exists, and its linear dimension is in fact propor-

tional to $\Delta(\partial\alpha/\partial\varphi)$. The surface for which $\Delta(\partial\alpha/\partial\varphi) \neq 0$ is obviously atomically smooth.

Let now $T \neq 0$. Each step contains then a certain equilibrium kink density that increases rapidly with temperature. The free energy of the step (the quantities α and β have in fact the meaning of free energy) decreases with rising temperature because of the rapid growth of the configurational entropy of the kinks, and at a certain temperature T_c it can vanish [29]. At $T > T_c$ the initial surface will contain a certain step density determined by the interaction between the steps. Since the number of steps on such a surface is not given, and is itself determined by the condition that the surface energy be a minimum, it follows that the effective free energy of the step, which is equal to the derivative of the total free energy with respect to the number of steps, is zero. In other words, $\Delta(\partial\alpha/\partial\varphi) = 0$ at $T > T_c$ and there is no flat section corresponding to the given orientation in the equilibrium shape. The crystal surface contains thus at $T > T_c$ a large number of steps of all possible configurations, and is therefore atomically rough. The change of the state of the surface from atomically smooth to atomically rough, inasmuch as it is accompanied by a vanishing of the mathematical singularity of the function $\alpha(\varphi)$, should obviously proceed via a phase transition. Such transitions are known as roughening transitions [29] as well as "faceting transitions" [30].

Surface phase transitions will be considered in detail in Sec. VI, and here we wish to call attention to the following circumstance. As already noted, the concept of a step retains its meaning in a quantum crystal. Consequently, the connection between the positiveness of the energy of the step and the discontinuities of the angular derivatives of the surface energy, i.e., the faceting of the crystal, also remains in force. It is important, however, that in a quantum crystal the energy of a step can be exactly zero even at zero temperature. In fact, we have seen in the preceding section that on a surface in a quantum-rough state the number of steps of each sort is not fixed, and is itself determined from the condition that the total energy be a minimum, exactly as in the case of a classical atomically rough surface. The only difference is that at $T = 0$ it makes no sense to distinguish between the energy and the free energy. Thus, the surface of a classical crystal can be atomically rough for thermal reasons, while that of a quantum crystal can be rough because of effects of quantum-mechanical delocalization. One can say that the stronger the quantum effects, the

smaller the number of crystal faces that remain in the classical atomically smooth state at $T = 0$, i.e., the smaller the number of flat sections that remain in the equilibrium faceting. As for the He⁴ crystals, the experimental data [23, 7] give grounds for assuming that at $T = 0$ the equilibrium shape is a hexagonal prism with rounded-off edges and corners, and with flat sections that coincide with the corresponding faces of the growth prism (we disregard here the highly unlikely possibility of the appearance of new flat sections at temperatures below 0.3 K).

The short shape relaxation times for He⁴ crystals permit a direct experimental measurement of the surface energy. Baitbar, Edwards, and Laroche [31] measured the surface energy of He⁴ crystals by a method similar to the usual "drop detachment" method used to measure the surface tension of liquids. Neglecting the anisotropy, they obtained $\alpha = 0.107\text{--}0.145$ erg/cm² at $T \approx 1.3$ K. At lower temperatures the method employed, as noted subsequently by the authors themselves [32], is unsuitable even for an estimate of the angle-averaged values of α , since crystal faceting sets in during the measurement process. Under these conditions, more success was obtained with experiments in which the equilibrium shape of the surface was investigated by direct optical methods, namely holography [23] and photograpy [7].

The equation describing the equilibrium shape of the crystal in a gravitational field can be obtained from the phase-equilibrium condition [33]

$$F_1 + P + \left(\alpha + \frac{\partial^2 \alpha}{\partial \varphi_1^2} \right) \frac{1}{R_1} + \left(\alpha + \frac{\partial^2 \alpha}{\partial \varphi_2^2} \right) \frac{1}{R_2} = \frac{\rho_1}{m} \mu_2 \quad (6)$$

where F_1 is the free energy per unit volume of the crystal, ρ_1 is its density, m is the mass of the atom, P is the pressure in the liquid near the surface, $\mu_2(P)$ is the chemical potential of the liquid, R_1 and R_2 are the principal curvature radii of the surface, and φ_1 and φ_2 are angles measured in the planes of the principal normal cross sections. We introduce a coordinate system x, y, z in which the crystal surface is described by the function $z = \zeta(x, y)$. We put $P = P_0 - \rho_2 K \zeta$ and $\mu_2 = \mu_2^0 - mg\zeta$, where ρ_2 is the density of the liquid. Then, considering for simplicity surface sections that are slightly inclined to the horizon-

tal, $\partial^2 \zeta / \partial x_\mu^2 \ll 1$, we obtain:

$$\left(\alpha \cdot \delta_{\mu\nu} + \frac{\partial^2 \alpha}{\partial q_\mu \partial q_\nu} \right) \frac{\partial^2 \zeta}{\partial x_\mu \partial x_\nu} - (\rho_1 - \rho_2) g \zeta = 0 \quad \mu, \nu = 1, 2. \quad (7)$$

The real shape of the crystal surface depends, of course, on the concrete geometry of the instrument and on the wetting angles on the boundary with the walls. The experimental data [31, 6, 23] show that solid helium wets poorly the surfaces of a great variety of materials: copper, ferrochrome, glass, capron (nylon), etc. For this reason, the equilibrium surface of the crystal takes usually the shape of a convex meniscus (Fig. 16). By choosing a suitable trial function $\zeta(x, y)$ for the description of the shape of the meniscus, we can in principle determine the quantity $\bar{\alpha} = \alpha \delta_{\mu\nu} + (\partial^2 \alpha / \partial q_\mu \partial q_\nu)$ corresponding to

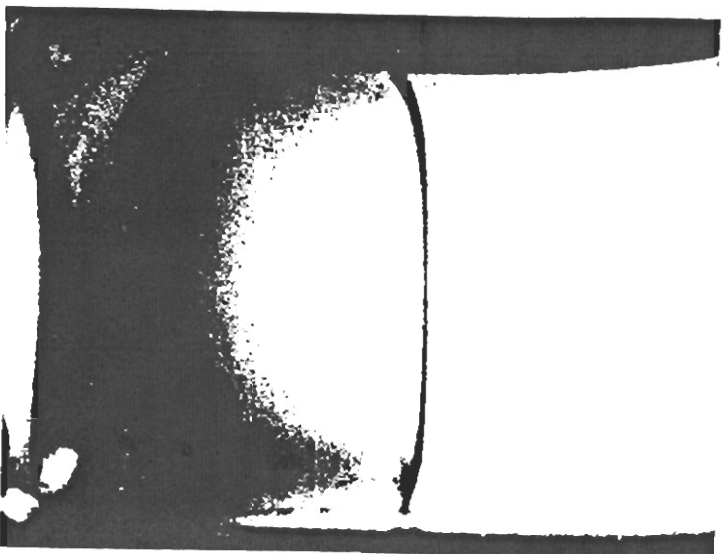


Figure 16. Equilibrium meniscus.

each given section of the surface, i.e., the eigenvalues and eigendirections of the tensor $\bar{\alpha}_{\mu\nu} = \alpha \delta_{\mu\nu} + (\partial^2 \alpha / \partial q_\mu \partial q_\nu)$. This method, however, calls for excessively detailed information on the shape of the surface, and has not been used in pure form to this day. In practice it is necessary to introduce a number of simplifying assumptions, and in particular to neglect the anisotropy of $\bar{\alpha}$ [23]. At the same time, even in the simplified form the method yields apparently reliable data on the temperature dependence of $\bar{\alpha}$ [17]. It was established in this manner that in the range 0.4–1.45 K the value of $\bar{\alpha}$ for different orientations of the surface ranges from 0.1 to 0.2 erg/cm², and is independent of temperature within the limits of measurement accuracy (~20%). This result applies to surfaces having a certain arbitrary orientation not too close to any one of the principal surfaces.

Particularly noteworthy is the case when one or both principal values of the tensor $\bar{\alpha}_{\mu\nu}$ become infinite. In this case, as seen from (6) and (7), one (or both) of the principal curvature radii becomes infinite, i.e., the surface has a cylindrical (or flat) section. We see thus that the gravitational field by itself does not lead to the vanishing of the flat section, including the inclined ones, but of course can strongly alter their dimensions and shapes. It is useful to note a simple relation between the dimensions of a flat section and the curvature a surface near its edge. Thus, for the case of a horizontal flat section in the form of a circle of radius $l/2$, Eq. (7), after integration along the diameter, yields

$$l = \frac{R}{\bar{\alpha}} \Delta \frac{\partial \alpha}{\partial \varphi} \quad (8)$$

where φ is the azimuthal angle, $\bar{\alpha} = \alpha + \partial^2 \alpha / \partial q^2$ and R pertain to the region adjacent to the edge of the flat section, i.e., as $\varphi \rightarrow 0$; K is the principal curvature radius (the second principal radius is infinite). Similar but more complicated expressions can be easily obtained also for other cases.

VI Phase Transitions on Helium-Crystal Surfaces

As already noted at low temperatures (lower than approximately 1.2 K) the equilibrium shape of a helium crystal contains, besides the

rounded sections, also flat ones. Under real conditions, the observation of the equilibrium shape is strongly complicated by the presence of the walls and of the gravitational field. The influence of the gravitational field is substantially reduced if the crystal dimension is small enough (less than capillary constant, which in the case of helium is ~ 1 mm), but in this case there is a stronger influence of the inhomogeneity of the substrate on which the crystal rests. In addition, the shapes of small crystals are more difficult to investigate quantitatively.

The faceting of a large crystal that fills at equilibrium the entire lower part of the container can, naturally, not be represented completely enough. If such a crystal has a random orientation relative to the gravitational field, then its surface, depending on the wetting angles, either contains no flat sections at all, or contains one or two such sections, which are small and are located near the walls. In such situations it is quite difficult to decide whether these specks are really

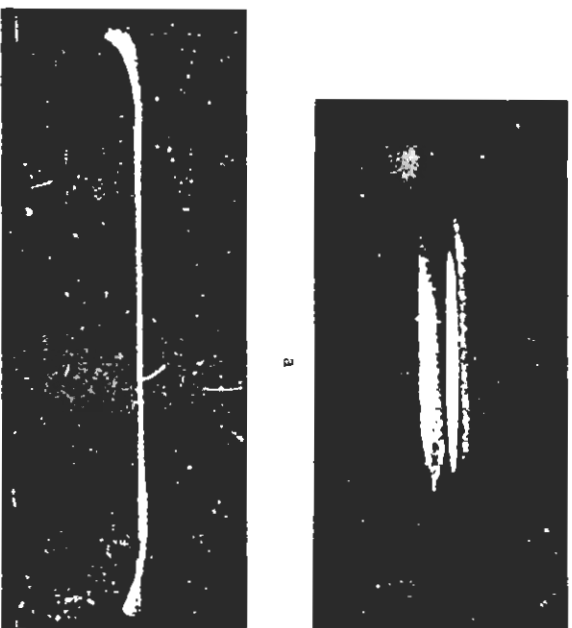


Figure 17. Shape of meniscus for crystal with horizontal (0001) plane: a—overall view, b—profile.

flat or whether their presence is merely a consequence of some crystal defect or of the container walls.

A qualitatively different picture is observed in cases when one of the "special" surfaces, i.e., the faces of the growth prism, is close to a horizontal plane [7]. In these cases, at sufficiently low temperatures, the equilibrium meniscus contains an ideally flat section (the possible curvature radius of such a "mirror" is not less than l^2/λ , where l is the dimension of the "mirror" and λ is the wavelength of the visible light). Figs. 17a and 17b. The "mirror" is surrounded on all sides by the rounded-off surface of the meniscus, which has the usual form. The plane of the "mirror" coincides exactly with one of the faces of the growth prism, as is readily established when such a crystal is grown.

It became possible to grow a crystal with a practically horizontal basal plane or with the lateral face of the growth prism by means of the following artifice. In those cases when the growth nucleus appears in one of the walls in the central or upper part of the chamber, it is frequently possible to "drop" it on a horizontal copper bottom by melting the crystal at the place of its contact with the wall. It suffices for this purpose to apply to the wall a small heating pulse with the aid of some external source, such as a flashlight. The temperature of the chamber should in this case be 0.8 K or a little bit higher. Next, in the drooping process, which lasts a fraction of a second, the crystal must grow somewhat and consequently become faceted.* As a result the crystal, just as dice, lands on one of its flat faces (with overwhelming probability on the (0001) face). In this method it is possible to orient the basal plane horizontally with accuracy better than 1° , whereas at the best of the "tossings" that end with "landing" of the lateral face of the prism, the angle with the horizontal amounted to two or three degrees.

In those cases when this artifice does not lead directly to success, e.g., because of an improper location of the nucleus, it helps to turn

*It is curious to note that such a drop lasts much more than the "bumpings" described in Sec. III, which are entirely due to melting and crystallization; the difference is particularly large at the lowest temperature. In other words, if the geometry of the apparatus permits it, then the crystal can grow much faster than "sinks" under the influence of the gravitational field. This is not surprising since, at the same boundary velocity, the total kinetic energy is much lower in the former case than in the latter.

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on an electric field. At a capacitor voltage exceeding 700–800 V, the nucleus is always produced on the capacitor surface,* from which it is possible to “drop” the crystals in most cases. To be sure, in this case several nuclei are produced almost simultaneously as a rule, and the above artifact must be carried out very rapidly.

Crystal growing from seeds oriented in such a way encounters the same difficulties as the growing of crystals with other orientations. The presence of visible defects greatly distorts the shape of the flat “mirror” decreases its size, and may cause it even to disappear completely. In addition, the shape and location of the “mirror” are most sensitive to even slight (several degrees) inclinations relative to the gravitational field.

With increasing temperature, the “mirror” decreases in size and disappears completely at a certain temperature T_c . The values of T_c for a given face vary noticeably (by 0.1–0.2 K) from sample to sample, probably depending on the degree of perfection of the crystal. It appears that the maximum values of T_c are reached in the most perfect crystals (maintaining the crystals for a long time at a temperature close to T_c leads to an increase of T_c). The highest of the registered values of T_c amount to 1.17 K for the basal plane and 0.9 K for a lateral face of the prism. In measurements of the temperature dependence of the size of the “mirror” in a relatively large temperature interval (several tenths of a degree Kelvin) the results are so poorly reproducible that no regular curve can be obtained at all. Greatest interest, however, attaches to the temperature dependence of the “mirror” size in the immediate vicinity of T_c . We have attempted to perform such measurements, by maintaining the crystal all the time, starting from the instant of its growth, near T_c . However, even in these experiments we were unable to achieve satisfactory reproducibility. Figure 18 shows the results of one such experiment. A crystal with the basal plane “laid” horizontally with accuracy better than 0.5° was grown at a temperature close to 1.15 K and was kept at 1.15–1.18 K for 15 hours. The dimension l was determined from the angle width of the principal diffraction maximum obtained by reflection

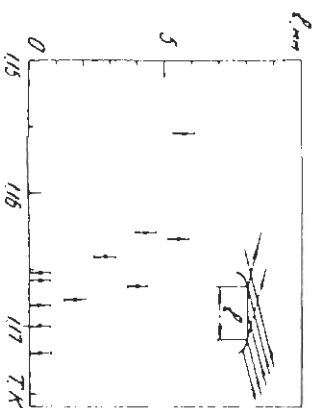


Figure 18 Temperature dependence of the size of the flat section.

tion of a plane-parallel light beam at an angle 5° from the meniscus with the “mirror” (see Fig. 18). Each measurement was made after the temperature was stabilized accurate to 10^{-4} K for at least a half an hour. After cooling the crystal to a temperature below 1 K, the measured dimension amounted to 9–10 μm . The causes of the observed scatter of the points are not sufficiently clear at present: it is possible that it is due to fluctuations of the amount of helium in the chamber or even to mechanical vibrations of the apparatus (we emphasize, that the “mirror” on the surface of the growing crystal is observed also at temperatures much higher than T_c for the given face). One cannot exclude, naturally, the possibility that the total shape relaxation time, including also the possible processes of crystal annealing, is too long.

Avron et al. [34] observed in their experiments the vanishing of the flat sections by a holographic technique. A small (about 2 mm) crystal was located in the lateral part of a cylindrical container: the crystal was so oriented that its faceting incorporated a basal plane (0001) and two crystallographically equivalent lateral prism faces. A jump-like vanishing of the lateral surface was observed, with the two equivalent faces vanishing at different temperatures, one at 0.8 K and the other at 0.9 K. With further increase of temperature, a decrease of the area of the (0001) face was observed, accompanied by a sudden change of the visible size of the crystal at 1.08 K. Unfortunately, it is not clear from the text of the article [34] whether the (0001) face vanishes completely at 1.08 K, and if it does, whether gradually or jumpwise. At any rate, the described data are difficult to reconcile

* Immediately prior to the formation of visible nuclei, the reflectivity of the capacitor surface under glancing illumination changes radically. This is, probably, due to the formation of a large number of small (1–10 μm) crystals in the region with the maximum field intensity.

with the assumption that thermodynamic-equilibrium phase transitions were observed in the described experiments.

It seems that the most serious difficulties of experimental investigations of faceting phase transitions are due to the need for ensuring an experimental situation sufficiently close to complete thermodynamic equilibrium. In this connection, we must emphasize the following. As is well known in ordinary crystallography, a distinction must be made between equilibrium faceting and the kinetic faceting resulting from the anisotropy of the growth rate. Generally speaking, the two types of faceting are far from identical. In particular, in the case of He^4 crystals, as already noted, the kinetic faceting is observed up to temperatures much higher (by at least 0.1 K) than the temperature of the faceting phase transition. This statement applies to each of the faces on which a phase transition is observed (we note that in principle, in a quantum crystal equilibrium faceting might not arise at all at any temperature, even in the presence of kinetic faceting). This fact, when account is taken of the very strong anisotropy of the He^4 crystal growth rate, forces us to interpret with great caution the results of experiments connected with observation, and all the more with quantitative investigation, of faceting phase transitions. Thus, it appears that it was precisely the kinetic faceting of helium crystals which manifested itself in the experiments of Balibar, Edwards, and Laroche [31].

It can thus be stated that experimental investigations of surface phase transitions in He^4 are at present only beginning. In essence, all we know at present (and possibly with insufficient accuracy) are the transition temperatures for both faces at which the transition is observed. The concept of phase transitions connected with the onset of faceting of the crystal was introduced into the theory first by Barton and Cabrera [29, 1], who regarded them as roughening transitions, i.e., as transitions from an atomically smooth to an atomically rough surface of a classical crystal. Since that time surface phase transitions were investigated in a rather large number of theoretical studies within the framework of some model of a two-dimensional phase transition [34-39]. At present, however, it is still too early to speak of the possibility of comparing any of these models with the experimental data on the faceting of He^4 crystals. Considerable interest attaches therefore to the question of the position occupied by faceting transitions in the general classification of phase transitions.

A phenomenological approach to the problem of a faceting phase transition was developed in a recent paper by Andreev [30]. Treating the phase transition point as a critical point at which the equilibrium shape of the crystal first loses stability as it varies continuously with temperature, Andreev arrived at the conclusion that faceting phase transitions having the meaning of second-order transitions are possible in a rather large class of cases. As applied to He^4 crystals, interest attaches to surfaces having a C_6 axis (basal plane) and C_2 axis (lateral faces of the prism). In the former case, according to Andreev, a flat section is produced at $T = T_c$ and is bordered by a circle whose radius is proportional to $\sqrt{T_c - T}$. In the second case the flat section either does not appear at all, or is produced in two stages: when the temperature is high, there is produced first at a certain temperature T_1 , a "cylindrical" section, i.e., a section with zero curvature in only one direction and then, at a temperature T_2 , a perfectly flat section can be produced. The equations of Andreev's theory are quite similar to the equations of the Landau theory of second-order transitions. Thus, at $T = T_c$ the heat capacity has a discontinuity on the singular face, whereas $\alpha(\varphi)$ on all the nearby faces is an analytic function, and the role of the order parameter is assumed by the discontinuity of the angular derivative $\Delta(\partial\alpha/\partial\varphi)$ or, equivalently, by the linear dimension of the section with zero curvature. When comparing the theory with experiment it is necessary, incidentally, to bear in mind that, to our knowledge, no "cylindrical" surfaces were observed so far in He^4 crystals.

Within the framework of the phenomenological approach, besides second-order transitions, it is possible to have in principle faceting transitions wherein the shape of the crystal varies continuously with temperature, and which have at the same time the features of first-order transitions. In fact, a first-order transition is characterized by the presence of two states, each of which is separately stable at a certain temperature interval near the transition temperature T_c . Let the surface energy of the first state $\alpha_1(T, \varphi)$ correspond to a fully rounded equilibrium shape, and let $\alpha_2(T, \varphi)$ have a discontinuous derivative $\partial\alpha_2/\partial\varphi$ at $\varphi = \varphi_0$ (with $\Delta(\partial\alpha_2/\partial\varphi)$ not equal to zero near T_c) and correspond thus to the presence of a flat section at $\varphi = \varphi_0$, in the equilibrium shape. Both functions α_1 and α_2 are certain smooth functions of the temperature. Let furthermore, $\alpha_2 > \alpha_1$ at $T > T_c$ for all angles φ , and let $\alpha_2 < \alpha_1$ in a certain angle interval near φ_0 at

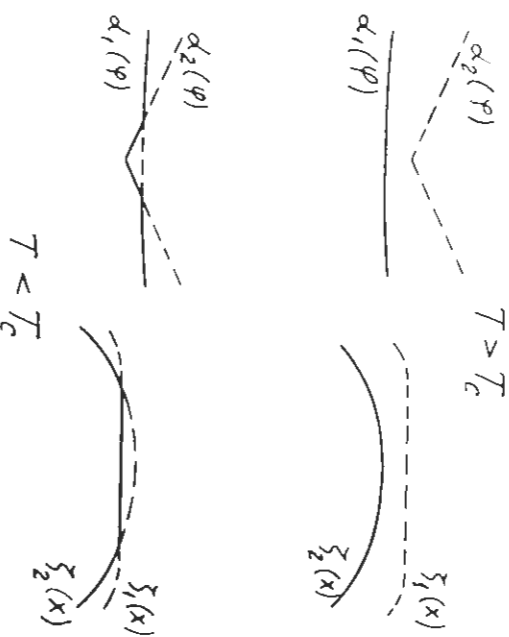


Figure 19 Surface energy and equilibrium shape of crystal in first-order phase transition.

$T < T_c$ (see Fig. 19). At $T > T_c$ the crystal will then be in a state with $\alpha = \alpha_1$, i.e., have a completely rounded shape. At $T < T_c$ the value of α is determined by the condition $\alpha(\varphi) = \min\{\alpha_1, \alpha_2\}$, and a flat section appears in the equilibrium shape (Fig. 19), with a dimension, as can be easily understood, that increases in proportion to $\sqrt{T_c - T}$. In contrast to second-order transitions, however, in this case there is an edge at the boundary of the flat section, i.e., the flat and rounded sections meet at a finite angle (likewise proportional to $\sqrt{T_c - T}$). In addition, in this case there is no connection between the discontinuity of the angular derivative $\Delta(\partial\alpha/\partial\varphi)$ and the dimension of the flat section. $\alpha(T)$ at the very transition point is continuous at $\varphi = \varphi_0$, and the entropy $(-\partial\alpha/\partial T)$ has a finite jump, as should be the case in a first-order transition.

As for transitions connected with a jumplike change of the shape of the surface, it can be easily seen that such a transition cannot take place at all in a thermodynamic-equilibrium manner*. In fact, the presence of such a transition at $T = T_c$ means the existence of two different functions $\alpha_1(T, \varphi)$ and $\alpha_2(T, \varphi)$ corresponding to two differ-

ent states that are separately stable near T_c . But in this case, as we have just seen, there is either no phase transition at all, or a phase transition of first order with continuous change of shape takes place. The only case when the equilibrium shape of the crystal can change jumpwise is when a first-order transition takes place in the bulk of the crystal.

As usual, the possibility of first-order faceting transitions is not governed by any symmetry considerations; thus, the foregoing reasoning is obviously valid for faces of any symmetry. Surface phase transitions, however, are subject to restrictions of a different character, connected with the possible striction instability [40, 41]. Thus, first-order transitions can be observed only in those cases when the striction effects are small enough (for more details see the papers of Marchenko [41, 42]). As for the experimental data pertaining to the He⁴ crystals, the appearance of edges in the equilibrium faceting has not been observed by any one to this day. Thus, Fig. 17b, which shows a photograph of the basal plane at $T \approx 0.5$ K, points quite clearly to the absence of such edges. We note that if really there are no edges in the equilibrium shape, then our experimental data allow us to estimate the step energy β by using Eq. (8). We shall assume for the sake of argument that the height of the elementary step on the (0001) plane is 3.5 Å, i.e., half the length of the elementary translation along the C_6 axis. We then obtain from Fig. 17 at low temperatures an order-of-magnitude value $\beta \sim 5 \cdot 10^{-9}$ erg/cm, and near T_c , say for $l = 4$ mm (Fig. 18), $\beta \sim 10^{-10}$ erg/cm. We note for comparison that Balibar and Castaing [32], in an interpretation of the experimental data of [31] in terms of the roughening transition, obtained $\beta \sim 7 \cdot 10^{-8}$ erg/cm. As for the lateral faces of the prism, we do not have in this case as clear a proof of the absence of edges as for the (0001) face, so that numerical estimates of any kind are premature in this case.

VII Crystallization Waves

We have seen in Sec. VI that a quantum-rough surface state ensures the possibility of an exactly nondissipative crystallization and melting of a crystal at $T = 0$. This possibility means that at sufficiently low temperatures the process of relaxation to an equilibrium crystal shape

(for the case of a quantum-rough surface) should be of oscillatory nature. In fact, any deviation of the crystal shape from equilibrium leads to an increase of the surface energy. Therefore any nonequilibrium crystal shape will tend to change in a way that decreases the surface energy via crystallization or melting. On the other hand, in view of the difference between the densities of the two phases, the growth and melting of the crystal causes motion of the liquid, i.e., an increase of the kinetic energy of the system. It is clear that if the energy dissipation is low, then the surface will undergo weakly damped oscillations, similar in many respects with the usual capillary waves on the surface of a liquid. The spectrum of these oscillations (crystallization waves) can be easily obtained in the long-wave limit, when the compressibilities of both phases can be neglected [5]. It is important that this does not call for invoking any model concepts concerning the microscopic structure of the surface.

In the derivation of the crystallization-wave spectrum we shall take into account the gravitational field and the damping due to the finite kinetic growth coefficient. To this end, we note first that when account is taken of capillary effect Eq. (6) replaces the usual phase-equilibrium condition $\mu_1 = \mu_2$. Therefore when describing weakly nonequilibrium situations, e.g., crystal growth in the absence of a heat flux, it is necessary to add to the right-hand of (6) the term— $\beta_1 V/mK$, where V is the growth rate at the given point and K is the kinetic growth coefficient. We consider next a flat surface $z = 0$ that undergoes a displacement $\xi(x, t) = \xi_0 \exp(ikx - i\omega t)$ in the direction of its normal. The motion that is produced in the incompressible liquid is described by a potential ψ that satisfies the Laplace equation $\nabla^2 \psi = 0$, i.e., $\psi = \psi_0 \exp(ikx - kz - i\omega t)$. Mass conservation in the phase transition yields the boundary condition for the z component of the velocity of the liquid:

$$V_z = \frac{\rho_2 - \rho_1}{\rho_2} \dot{\xi} \quad \text{at } z = 0 \quad (9)$$

and the phase-equilibrium condition (6) should be replaced in this case by

$$\left(\frac{1}{\rho_2} - \frac{1}{\rho_1} \right) (\rho_1 - \rho_2 g \xi) + \frac{1}{\rho_1} \alpha \frac{\partial^2 \xi}{\partial x^2} = \frac{1}{mK} \dot{\xi} \quad (10)$$

where $\tilde{\alpha} = \alpha + (\partial^2 \alpha / \partial \varphi^2)$, φ is the angle between the normal to the shifted surface and the z axis, P' is the variable part of the pressure in the liquid (we take into account here the fact that $\partial \mu_2 / \partial P = m/\rho_2$). Next, recognizing that

$$P' = -\rho_2 \dot{\psi}, \quad \bar{\nabla} = \nabla \psi \quad (a)$$

we obtain the spectrum of the plane waves

$$\omega^2 - \frac{\tilde{\alpha} \rho_2}{(\rho_1 - \rho_2)^2} k^3 - \frac{\rho_2 k}{\rho_1 - \rho_2} g + \frac{\rho_1 \rho_2}{(\rho_1 - \rho_2)^2} \frac{i\omega k}{mK} = 0 \quad (11)$$

As seen from (11), the propagation velocity of these oscillations is much lower than the sound velocity, thus justifying the neglect of the compressibilities of the two phases in the derivation. The gravitational term in (11), just as for ordinary capillary waves, must be taken into account only at the very lowest frequencies, when the wavelength becomes of the order of or larger than the capillary constant (~ 1 mm).

Just as ordinary capillary waves, crystallization waves are unstable to the decay of one quantum into two with a lower energy. Therefore, strictly speaking, they have a finite damping even at $T = 0$, when $K \rightarrow \infty$. The order of magnitude of this damping (the reciprocal lifetime) γ is given by the formula $\gamma \sim \hbar k^5 / \rho$ (see [43], where the corresponding problem was solved for ordinary capillary waves). At finite temperatures the most important for low-frequency oscillations is the damping mechanism due to the finite value of the growth coefficient K . From (11), assuming the damping to be small, we obtain

$$\gamma = \frac{\rho_1 \rho_2 k}{2mK(\rho_1 - \rho_2)^2} \quad (12)$$

In the case of He^3 , in the region where the Fermi-liquid theory is applicable, the use of the estimate given in Sec. IV for the value of K shows that the oscillation in question attenuates strongly at all frequencies. Leading to the same conclusion, of course, is also an estimate of this quantity for a classical crystal that has an atomically rough surface, according to (2). Obviously, there can be no linear

oscillations of the crystallization-wave type at all on a classical atomically smooth surface. Thus, the existence of weakly damped crystallization and melting waves is essentially a quantum effect.

In practice it is easiest to excite a crystallization wave in He^4 by purely mechanical means, as incidentally the case for an ordinary capillar wave on the surface of a liquid. This is in fact how crystallization waves were first observed [6]. It turned out that even an insignificant vibration of the apparatus is sufficient for the excitation of visible surface oscillations. Knocking on the outer wall of the cryostat produced oscillations of amplitude 1–2 mm. Figs. 20a, b, c, d show

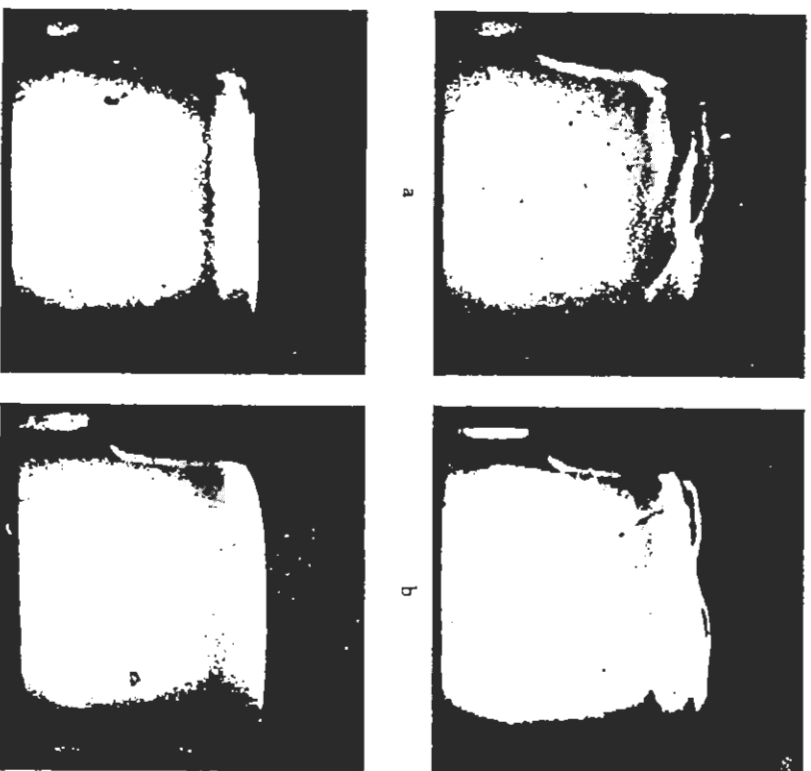


Figure 20 Motion picture of excitation and attenuation of crystallization waves.

motion-picture frames of the excitation and damping of the oscillations. The first frame shows the quiescent boundary between the solid (lower) phase and the liquid. The succeeding frames demonstrate the behavior of the boundary following a knock on the outer wall of the cryostat. Such oscillations are easily observed at temperatures 0.4–0.6 K. With increasing temperature, the amplitude of the oscillations decreases rapidly, and they cannot be excited in practice by the method indicated already at 0.8 K.

In the case when the equilibrium meniscus contains one of the singular boundaries which remains flat, the oscillations are observed only on the rounded sections of the meniscus, whereas the flat section remains perfectly immobile, and only its boundary oscillates due to the oscillations of the rounded-off sections. If the oscillation amplitude is very large, terraces can be produced on the flat sections. They move rapidly over the flat section but their height remains unchanged (similar terraces are sometimes observed in the case of rapid growth of the crystal (Fig. 21)). We note finally that crystallization waves are observed not only under quasi-equilibrium conditions, when the crystal fills the entire lower part of the container, but also, e.g., in situations when the crystal "hangs" from one of the side walls of the container (Fig. 7). In this case oscillations are clearly seen on the rounded sections, and only on them. All these data demonstrate once more the difference between the behavior of quantum-rough and classical atomically smooth surfaces at low temperatures.

To measure the spectrum of the crystallization waves it is necessary to excite a plane wave. In [6, 7] a capacitor was used for this purpose



Figure 21 Terraces on the basal plane.

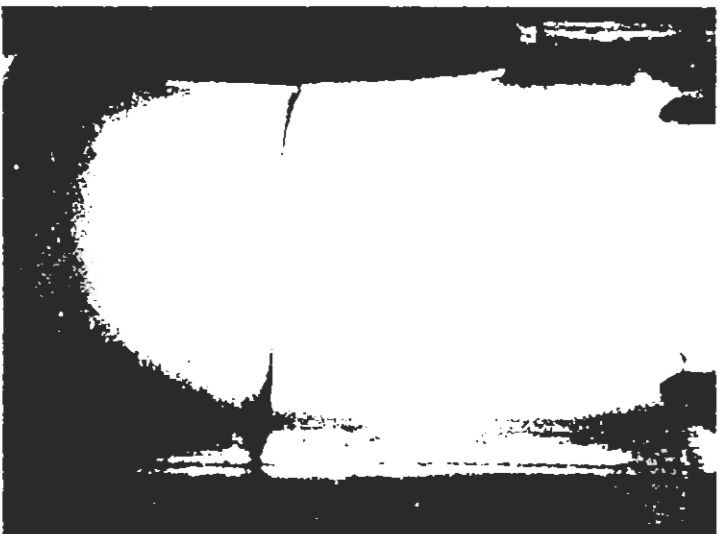


Figure 22 Crystal surface in an electric field.

and was mounted on one of the side walls of the container. A constant voltage applied to the capacitor caused a visible change in the wetting angle and a corresponding rise in the edge of the meniscus adjacent to the capacitor (Fig. 22). This rise can reach 1–2 mm. At low voltages, the rise is approximately proportional to the square of the voltage, and starting with 0.8–1.0 kV this dependence saturates rapidly. This saturation is due apparently to the already mentioned onset of small crystals on the surface of the capacitor, which crowd out the main crystal from the regions with the maximum field. Accordingly, the efficiency of excitation of the surface oscillations by the alternating field is decreased in the saturation region.

When an alternating voltage of suitable frequency is applied to the capacitor, a plane crystallization wave with wave vector \mathbf{k} normal to the capacitor plates is excited. Depending on the frequency, it is

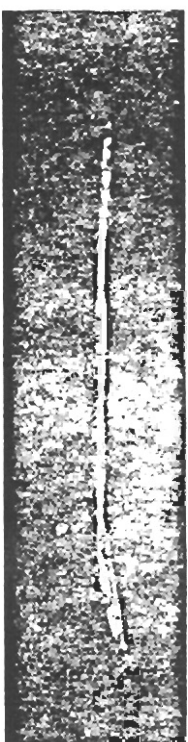


Figure 23 Standing crystallization wave.

possible to excite a standing as well as a traveling wave. Standing waves with amplitudes large enough to be photographed could be excited only at relatively low frequencies (below 100 Hz; see Fig. 23). The strong deviation of the resonator made up by the crystal surface and the sidewalls of the container from ideal, and the presence of natural mechanical frequencies of the apparatus in the same band, made it impossible to use standing waves in accurate measurements of the spectrum. Higher frequencies, up to several kHz, were therefore used in such measurements. At still higher frequencies, the amplitudes of the excited traveling waves were already too small to be able to measure reliably the wavelength by the methods used by us. In the first experiments [6] the wavelength of the crystallization waves was measured by using the diffraction of light from an He-Ne laser by these waves. This method turned out to be inconvenient in practice, primarily because of the presence of random surface oscillations due to vibrations of the apparatus; in addition, it does not make it possible to measure the attenuation.

This was followed by a method [7] in which a narrow laser beam (naturally, much narrower than the measured wavelength) scanned slowly the oscillating surface, remaining practically parallel to the wavefront. The vertical beam dimension was approximately 2 mm, the wave amplitude was estimated at 0.01–0.05 mm, and the amplitude of the random oscillations was of the same order or even somewhat larger. The lower part of the beam was refracted by the slightly bent surface and was deflected downward considerably. The remaining light, passing over the surface, was incident on a photodiode. Thus, the intensity of the light on the photodiode contains an alternating component proportional to the vertical displacement of the surface at the given point. The signal from the photodiode was amplified by a selective amplifier tuned to the excita-

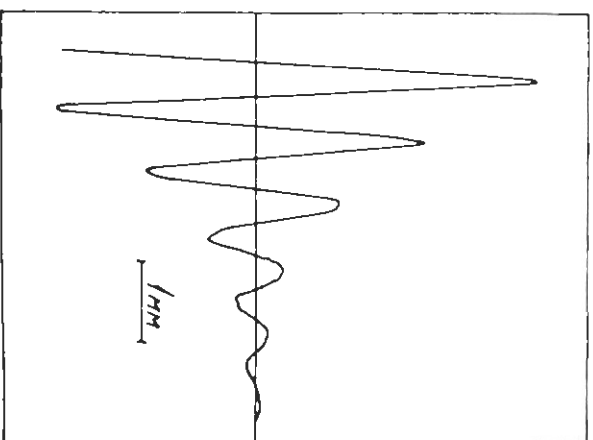


Figure 24 Typical experimental plot.

tion frequency, and after passing through a lock-in detector (at a constant phase shift between the exciting and reference signals) was fed to the Y input of an $X-Y$ recorder. The voltage on the capacitor consisted actually of a dc U_1 and ac (with frequency ω) voltage U_2 , with $U_1 \gg U_2$. The X input of the recorder received simultaneously a signal from a multiturn potentiometer coupled to a micrometer screw with which the scanning was effected. Fig. 24 shows one of the plots obtained by this method.

The distance between the signal zeroes along the X axis determines the length of the crystallization wave, and the ratio of the amplitudes of the neighboring maxima determines its attenuation. Figure 25 shows the results of the measurement of the spectrum for one of our samples at two temperatures, 0.360 and 0.505 K. The dashed straight line corresponds to the plot of $\omega \propto k^{3/2}$, and the solid curve is the theoretical plot of $\omega(k)$ according to Eq. (11) with account taken of the gravitational term (the correction for the attenuation can be neglected) and with $\bar{\alpha} = 0.21$ erg/cm². Thus, within the accuracy limits (5%), $\bar{\alpha}$ remains unchanged when the temperature is raised from

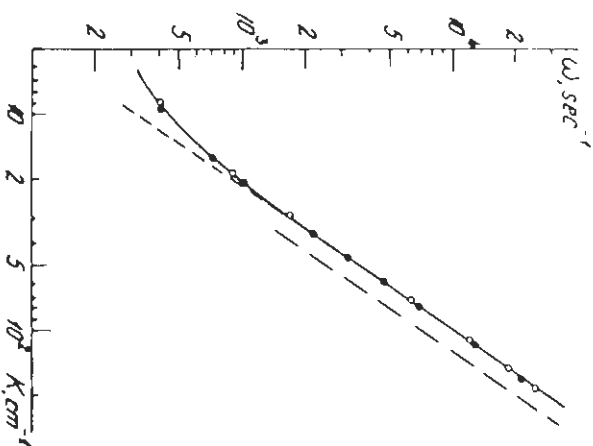


Figure 25 Spectrum of crystallization waves. Sample No. 1, ●— $T = 0.505$ K, ○— $T = 0.360$ K, $\bar{\alpha} = 0.21$ erg/cm². Sample No. 2—Dash-dot line, $\bar{\alpha} = 0.097$ erg/cm².

0.36 K to 0.50 K. The data for other samples agree in essence with those presented, differing only in a small overall shift, corresponding to a changed value of $\bar{\alpha}$, of the entire curve. In addition to the foregoing, we registered the following values of $\bar{\alpha}$: 0.18, 0.15, and 0.097 erg/cm² (dash-dot straight line on Fig. 25). The spectrum given in [6] corresponds to $\bar{\alpha} = 0.23 \pm 0.04$ erg/cm². These data offer evidence of the presence of a substantial anisotropy of the surface energy α , but give, of course, no complete idea whatever on the magnitude and character of this anisotropy, since all the surfaces investigated by this method had a certain random orientation and made angles not less than 20° with any of the special surfaces.

Measurement of the spectrum of the crystallization waves can be regarded as one of the possible methods of investigating the surface energy of He⁴ crystals. In practice this method ensures apparently a noticeably better accuracy compared with the direct investigation of the equilibrium shape, which was described in the preceding section. This applies in particular to investigations of the anisotropy of the

surface energy. Unfortunately, the rapid growth of the attenuation of the crystallization waves with temperature limits strongly the possibilities of investigating the temperature dependence of α by this method.

The theoretical temperature dependence of α can be obtained from the following considerations. The quantity α is the free energy per unit area of a surface having a given orientation. Its temperature dependence can be calculated if the spectrum of the elementary excitations of the surface is known. In our case the elementary excitations are collective excitations in a system of strongly interacting kinks and steps, i.e., crystallization waves. Of course, the spectrum of the crystallization waves takes the form (11) only at wavelengths that are large compared with the interatomic distance; the thermodynamic properties of the surface at low temperatures, however, are determined precisely by the long-wave, i.e., the low-frequency region of the spectrum. Inasmuch as in accord with (11) the frequency, just as in the case of capillary waves on a liquid-vapor interface, is proportional to $k^{3/2}$, the temperature dependence of the surface energy on a crystal-liquid interface at low temperatures is the same as on a liquid-vapor interface. According to Atkins [44], the temperature-dependent part of the surface energy is proportional to $T^{7/3}$. Numerical estimates show that for He^4 crystals the temperature dependence of α is too weak to be noticeable at the presently attained measurement accuracy.

Returning to the experimental investigations of crystallization waves, we note that in measurements of the spectrum and, in particular, of the damping of crystallization waves it is necessary to satisfy a number of rather stringent requirements. First, the amplitude of the wave must be small and furthermore the usual requirement that the amplitude be small compared with the wavelength is insufficient: at high voltages, as already mentioned, the crystallization takes place over the entire surface of the capacitor above the principal meniscus, the total volume of the liquid in the container changes periodically, and the resultant oscillation of the surface is a superposition of the investigated wave and of a quasihomogeneous oscillation of the same frequency. In addition, at large excitation amplitudes the results are no longer reproducible; this is due apparently to the irreversible changes that take place in the crystal when it is acted upon for a long time by an alternating electric field of large amplitude. Next, the wavelength must be small compared with the container dimension L ,

but large compared with the diameter of the capacitor-winding wire (0.04 mm). Finally, the damping must be not too large ($\kappa \approx k_0 \lambda$, where κ and k_0 are respectively the imaginary and real parts of the wave vector k), but also not too small ($\kappa L \gtrsim 1$), to be able to neglect the reflected wave.

In measurements of the attenuation (i.e., of the value of κ), since they involve measurements of the amplitude, another difficulty arises because of the imperfection of our optical system (primarily dirt on the glasses). Namely, the measured values can contain a small (~ 0.5 cm $^{-1}$) uncontrollable additive increment, due to the impossibility of exactly calibrating the transmission through the entire optical channel in each experiment.

The attenuation, as follows from (11), is determined by the relation

$$\kappa = \frac{1}{3} \rho_1 \rho_2^{1/2} (\rho_1 - \rho_2)^{-2/3} \alpha^{-2/3} (\omega m K)^{-1} \omega^{1/3} \quad (13)$$

(the gravitational correction can be neglected in the investigated frequency band). Figure 26 shows the results of the measurement of the frequency dependence of κ at two equal temperatures, for a

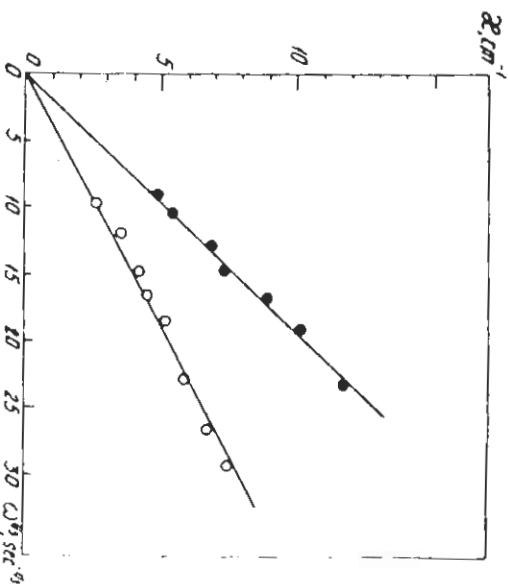


Figure 26. Frequency dependence of the attenuation of crystallization waves at two temperatures: O— $T = 0.360$ K, ●— $T = 0.505$ K.

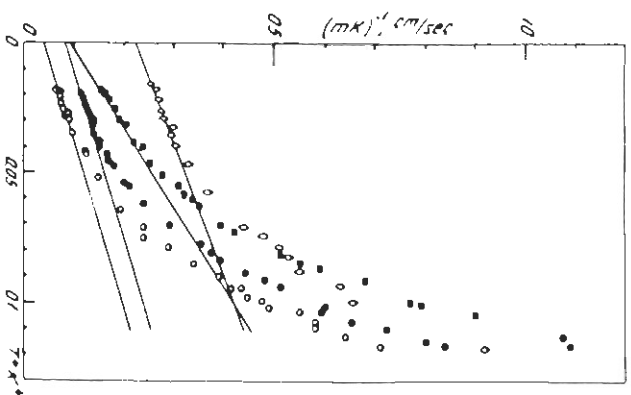


Figure 27. Temperature dependence of the damping of crystallization waves: Sample No. 3, O—1118 Hz; ●—232 Hz; Sample No. 4, ■—827 Hz; Sample No. 5, ○—837 Hz.

sample whose spectrum is shown in Fig. 25. It is seen that the relation $\kappa \propto \omega^{1/3}$ is indeed satisfied, i.e., the observed attenuation is indeed due to the finite character of the growth coefficient K .

According to Eq. (3) at low temperatures, when the energy dissipation produced when the interphase boundary moves is due to the collision between the boundary and the phonons, the growth coefficient depends on the temperature like $K \propto T^{-4}$, and at higher temperatures, when the number of rotons in the liquid become large enough, the dependence is given mainly by $K \propto \exp(\Delta_r/T)$, where Δ_r is the roton gap. Figure 27 demonstrates the temperature dependence of the quantity $1/mK$ calculated from the measured values of κ for three different samples.

It can be stated that at low temperatures the attenuation decreases more slowly than it would in the case of a pure phonon mechanism. When the experimental data are compared with the theory, it must be

kept in mind, however, that in a real experiment there are always reasons for residual attenuation, i.e., for a finite attenuation at arbitrarily low temperatures. These include various processes of the scattering of the crystallization waves by crystal defects and by surface vibrations, due to vibrations of the apparatus, the influence of the geometry of the radiator and of the curvature of the meniscus, and others. Thus, residual attenuation can obviously vary greatly from sample to sample, and depending on the specific scattering mechanism, vary with frequency in accordance with some law. From this point of view it is easy to explain the systematic discrepancies between the data corresponding to two different frequencies for sample 3 in Fig. 27 (the uncontrollable increment to the damping, which was mentioned above, is insufficient to explain this discrepancy).

The considerations advanced make it possible to interpret the data of Fig. 27 in the following manner. We assume that the measured attenuation consists of three independent terms: residual attenuation, as well as phonon and roton attenuation:

$$\frac{1}{mK} = A(\omega) + BT^4 + C \exp\left(-\frac{\Delta_r}{T}\right) \quad (14)$$

where, according to the foregoing, the coefficient A can vary from sample to sample and in addition depend on the frequency. The phonon damping B , owing to the strong anisotropy of the speed of sound in crystalline He^4 , can vary noticeably with the orientation of the sample. As for the roton contribution C , which depends mainly on the characteristics of the rotons of the liquid, it should apparently be the same for all the samples.

In accordance with this interpretation, straight lines were drawn in Fig. 27, representing the contributions of the first two terms in Eq. (14). The roton contribution determined in this manner is shown in Fig. 28. It is seen that all the data can be fitted in practice to a single dependence in the form $\exp(-\Delta/T)$. This is in essence the strongest argument favoring the advanced interpretation. The obtained value $\Delta = 7.8$ K is somewhat higher than that obtained from neutron-diffraction data (7.0–7.2 K) [45]. This difference, however, may be only apparent, since the coefficient C can depend on the temperature

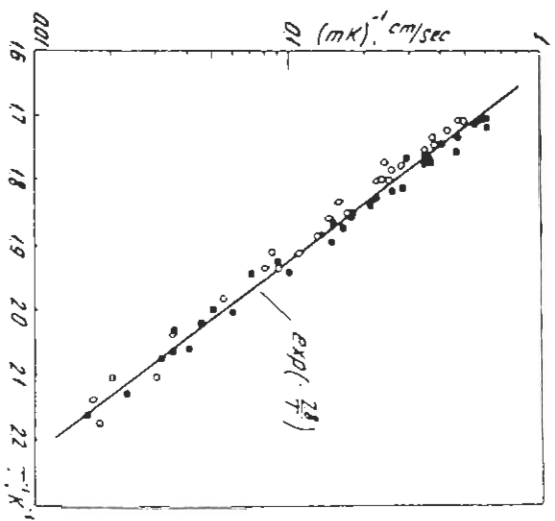


Figure 28. Roton contribution to the attenuation of crystallization waves. The symbols are the same as in Fig. 27. The straight line corresponds to $\Delta = 7.8$ K.

in accordance with some power law, as are most quantities that are determined by the roton spectrum (heat capacity, normal density, and others).

It would be quite interesting to compare these results with some other experimental data concerning the kinetic growth coefficient of He^4 crystals. Of course, the growth coefficient can in principle be measured directly. It would be sufficient for this purpose, e.g., simply measure with the required accuracy the pressure of the liquid over the surface of a crystal that grows at a known rate. For quantum-rough surfaces such measurements, however, require excessively sensitive pressure pickups: for atomically smooth surfaces, on the contrary, such measurements seem quite realistic. We note in this connection that if $\bar{\alpha}$ is known the values of the growth coefficient can be obtained from the measured crystal shape relaxation time. However, no such measurements were performed to this day.

An interesting method of investigating the growth kinetics of He^4 crystals was proposed by Castaing and Nozieres [46]. They have noted that ultrafast crystallization of helium leads to an anomalously

strong reflection of sound from the crystal-liquid interface. In fact, if $K \rightarrow \infty$, then when a sound wave is incident from the liquid on the interface, the condition $\mu_1 = \mu_2$ is satisfied, i.e., the pressure remains constant (if thermal effects can be neglected). In other words, owing to the rapid recrystallization, the oscillations of the pressure in the sound wave are not transmitted through the interface, i.e., the sound is totally reflected. On the other hand, if the growth coefficient K has a large but finite value, part of the sound process through the interface, and the amplitude of the transmitted sound is inversely proportional to K . Experiments based on this idea was performed by Castaing, Balibar, and Laroche [47]. In the range 0.4–1 K they obtained an exponential dependence of K on the temperature, with Δ ranging from 5 to 7.8 K for different samples. In these experiments they determined, simultaneously with the sound transmission coefficient, also the orientation of the crystal, or more accurately speaking the angle θ between the C_6 axis and the normal to the surface, by determining the time of passage of a sound pulse from the radiator to the receiver. The same method was used by the authors to verify the absence of blocks with different orientations. Such a method, however, is not suitable for the observation of stacking faults, to the formation of which, as already mentioned, large helium crystals have a considerable tendency. Yet the presence of stacking faults that emerge to the surface change its state substantially: the surface becomes hilly, and this leads to scattering of the sound. In addition, the surface defects slow down the crystallization processes, and this leads to a decrease of the effective growth coefficient. In addition, as already noted in Sec. III, merely a change in the crystal temperature within the measurement range frequently leads to irreversible changes of its surface. These changes can cause hysteresis phenomena in measurements of K , as noted by the authors of [47] themselves. It is difficult to say at present how much this circumstance has influenced the results. At any rate, it would be quite interesting to repeat the measurements of Castaing, Balibar, and Laroche under conditions that permit a direct control of the state of the surface.

Total reflection of sound from a quantum boundary can take place only in the case of normal incidence of the sound wave on the boundary. If the wave impinges on the boundary at a certain angle, then the "ripples" produced on the surface cause pressure oscillations even in the presence of phase equilibrium (see Eq. (6)). The conditions

for mechanical equilibrium of the surface [25] make it possible to determine the internal stresses that are produced in this case in the crystal. Thus, in the case of oblique incidence, the sound penetrates partially in the crystal, and the amplitude of the transmitted wave is proportional to the frequency [48]. The transmission coefficients depends, besides the elastic constants and the surface energy, also on the components of the so-called surface-stress tensor [33, 25]. This circumstance makes it possible, in principle, to measure the components of this tensor. Next, anomalously strong reflection of the sound from a quantum surface leads to anomalously large values of the Kapitza resistance at low temperatures. Since the phonon transmission probability is proportional to the square of the frequency, the Kapitza resistance, as can be easily seen, turns out to be proportional to T^{-5} .

We note finally that ordinary Rayleigh waves are present on the quantum surfaces of a helium crystal, and their spectrum is determined only by the properties of the crystal, just as in the case of the interface with vacuum [48]. Allowance for capillary effects could lead only to dispersion of their velocity, but not to attenuation, since the sound velocity in liquid helium exceeds the velocity of the transverse waves in the crystal. At the same time, on classical faces the velocity of the surface sound waves depends essentially on the properties of the liquid, see [49]. The Kapitza resistance on such faces should depend on the temperature in the usual manner, i.e., in proportion to T^{-3} .

Conclusion

The existence of weakly damped surface oscillations of helium crystals, due to periodic melting and crystallization, means that quantum effects play the decisive role in the crystallization of helium at low temperature. In essence, we are dealing here with a new macroscopic quantum phenomenon, namely a coherent phase transition. In fact, strictly nondissipative crystallization is possible only in the presence of a special type of coherent motion in a two-phase system, in contrast to the classical case, when crystallization is the result of random transitions of individual particles from one phase to another.

Of course, the current theory cannot claim to describe completely this phenomenon, it is in essence only a correct guess of its nature.

With increasing temperature, the role of the quantum effects, generally speaking, decreases. It is of interest to estimate the temperature region in which quantum effects are significant in the crystallization of helium. To this end we use the following simple arguments. We note that the quantum effects, at any rate, cannot be neglected if there exists at a given temperature a wavelength region in which the crystallization waves are weakly damped. The temperature T_0 above which the damping is large for all the wavelengths, up to atomic, can be estimated by extrapolating the data of Fig. 28 and using relation (13). Such an estimate yields $T_0 = 1.5$ K. In other words, everywhere, up to the transition into the bcc phase (and perhaps even higher), the processes that take place on the surface of a helium crystal are essentially of quantum nature.

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