

## **On the Interface at the Equilibrium Crystallization**

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Properties of an interface, created at some experimental conditions in the course of the equilibrium crystallization process, are theoretically investigated. Influence of quantum and thermal fluctuations on smoothing-roughening phase transitions is considered. The phase diagram illustrating these properties is found.

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**KEY WORDS:** Interface; equilibrium crystallization; crystal shape; roughening transition; surface tension; bifurcation set; transfer-matrix method; critical behavior; vicinal face.

The infatigable activity of Ilya Mikhailovitch Lifshitz, his bright talent and keen interest in the science have largely defined the modern state of condensed matter theory in many fundamental aspects. His impressive personality was no less wonderful than his scientific gift. Certainly he noted infelicities of a scientific work presented to him and subjected it to a necessary and benevolent criticism. But the first movement of his soul was invariant: he wished his opponent to be right. He was happy with the success of another person as much as some people are with their own success. This paper is our tribute to his fond memory.

### **1. INTRODUCTION**

In his well-known work<sup>(1)</sup> Landau has shown that the surface tension of a crystal is a nonanalytic function of the angles, which fix a face orientation with respect to the crystal axes. The existence of smooth areas of a crystal shape is a consequence of this nonanalytic behavior. Landau has considered faces of a type  $(0, 1, p)$  with large  $p$ s. They are vicinal to the face  $(0, 0, 1)$

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and have a periodic structure of steps. Every step is assumed to have a unit height. The spacing between the nearest steps is  $p$ . For a step to be formed some energy is required which leads to a jump of the surface energy derivative over the angle for the face  $(0, 0, 1)$ . The interaction between steps leads to singularities at the faces  $(0, 1, p)$  and at more complicated faces, for instance  $(0, 2, 2p - 1)$ . More complicated faces have been considered in the work by Bol'shov *et al.*<sup>(2)</sup> All these calculations are relevant to a classical system of steps at zero temperature, since both quantum fluctuations induced by bends of steps and thermal fluctuations have been ignored. The estimate of the contribution of quantum fluctuations on the interface structure has been made by Andreev and Parshin<sup>(3)</sup> in connection with the existence of crystallization waves. The qualitative estimate of thermal fluctuations has been given by Marchenko.<sup>(4)</sup>

A heightened interest in the problem of the equilibrium crystallization is associated with the experimental discovery of crystallization waves by Keshishev *et al.*<sup>(5)</sup> and with the subsequent experimental investigation of the interface between liquid and solid  ${}^4\text{He}$ .<sup>(6,7)</sup> Recently, a rather interesting experiment<sup>(8)</sup> revealing the ordering of the specific lateral face has been performed.

In this work we analyze the problem of the existence of vicinal faces and their structures. In Section 2 the influence of quantum effects on the existence of smooth and rough areas of the interface is considered. In principle at zero temperature an infinite branching sequence of smoothed segments in a crystal shape has to be expected. Their successions, sizes, etc. are elucidated in Section 3. Generally in a real experiment the structure period of a smoothed face must be limited to 20–30 lattice constants due to a finite size of a sample. The roughening transitions on vicinal faces induced by thermal fluctuations are considered in Section 4. The problem of the equilibrium shape of a crystal in gravitational field is the topic of Section 5. Recently an analogous question has been investigated by Avron *et al.*<sup>(9)</sup> Our calculations of Section 5 are similar to those of work Ref. 9, differing by the assumed geometry of the objects in question.

## 2. QUANTUM FLUCTUATIONS OF STEPS

For the sake of simplicity we assume that the face  $(0, 0, 1)$  has a simple square lattice. We restrict ourselves to the case of plane geometry when the matter is placed into the space between two parallel plates, or more generally is limited by a cylindrical surface. Under the above conditions the interface consists of faces of a type  $(0, m, n)$ . Every face can be treated as a periodic sequence of steps. First we consider properties of individual steps. The potential energy is minimal when a step has a form of a straight line. Kinks

can appear on a step as a result of quantum fluctuations. The pair kink–antikink can result from the adsorption of a “liquid” atom by a step at its smooth segment or vice versa. A living kink can move by a unit length along a step either absorbing an atom from the liquid phase, or desorbing an atom to the liquid. The simplest model corresponding to the above-mentioned quantum processes is described by a spin-1 Hamiltonian:

$$\mathcal{H}_0 = -\lambda \sum_m (S_m^+ S_{m+1}^- + S_m^- S_{m+1}^+) + \Delta \sum_m (S_m^z)^2 \quad (1)$$

where the spin projections  $S^z = \pm 1$  correspond to a kink and an antikink. The projection  $S^z = 0$  corresponds to a smooth sector on the step. The quantity  $\lambda$  is the quantum amplitude of atom arrival and departure processes.  $\Delta$  is a kink energy. At a small quantum parameter  $\lambda/\Delta \ll 1$  there is a gap in an elementary excitation spectrum. As a consequence the mean square displacement of the step  $\langle u^2 \rangle$  is finite. For large values of the quantum parameter the spectrum is gapless and the step meanders in a diffusionlike way. Its mean square displacement increases with the length  $L$  along the step as  $\langle u^2(L) \rangle \sim \ln L$ .

It should be noted that in the case of a more general vicinal face of the type  $(l, m, n)$  with  $l \ll m \ll n$  the steps are tilted and contain an extra concentration of kinks (antikinks)  $c = l/m$ . The quantum behavior of a such tilted step can be described by the Hamiltonian:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 \quad (2)$$

The additional term  $\mathcal{H}_1$  contains two important contributions. The first one is proportional to the field, thermodynamically conjugated to the concentration  $c$ . The second term is associated with the interaction of kinks. This interaction is assumed to decrease with a distance in a powerlike way with the exponent equal to 4 for van der Waals forces and equal to 3 for elastic forces:

$$\mathcal{H}_1 = -h \sum_m S_m^z + \sum_{m,n} V(n) S_m^z S_{m+n}^z \quad (3)$$

The phase diagram of the model with the Hamiltonian (2) is shown in Fig. 1. The dotted lines correspond to a fixed concentration  $c$ . The critical value of  $\lambda/\Delta$  at the transition to the gapless regime at fixed  $c$  is proportional to  $d^z V/dp^2|_{p=1/c}$ . In the gapless region a tilted step is smeared over the crystal as well as a nontilted step.

The situation becomes quite different when steps form a two-

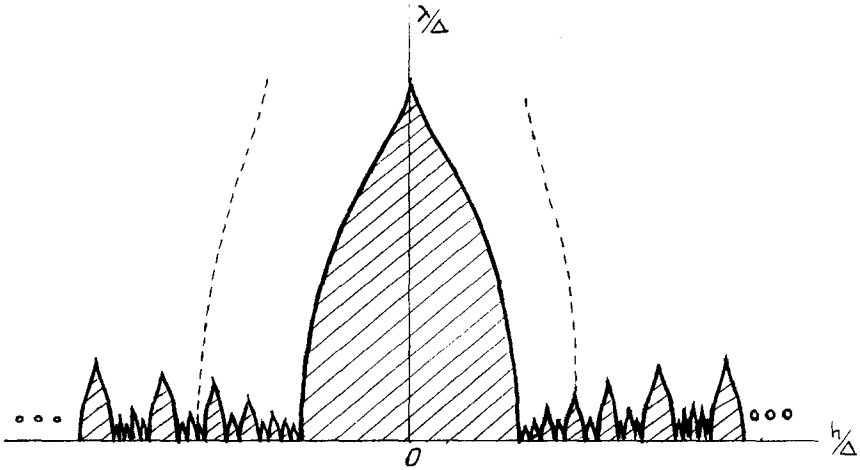


Fig. 1. Phase diagram of the model, described by the Hamiltonian (2). In the shaded area a step is pinned by the crystal potential. Constant slopes of the step are designated by dotted lines.

dimensional system. If they are situated sufficiently far from each other, the displacement  $\langle u^2 \rangle$  induced by fluctuations can be evaluated as follows:

$$\langle u^2 \rangle = a \int \frac{dq}{2\pi} \frac{\hbar}{2Msq} \sim \frac{a}{4\pi} \frac{\hbar}{Ms} \ln \frac{l}{a} \quad (4)$$

where  $a$  is a lattice constant;  $M$  is the atomic mass;  $s$  is the velocity of "sound" along an isolated step, which is assumed to be of the order of magnitude of the velocity of sound in the bulk crystal;  $l$  is a spacing between steps. The prelogarithmic factor in the right-hand side of Eq. (4) can be suitably represented as:  $\sim 0.1a^2(T_\lambda/\theta_D)$ , where  $T_\lambda$  is the  $\lambda$ -transition temperature,  $\theta_D$  is the Debye temperature. Assuming that the ratio  $T_\lambda/\theta_D \sim 0.1$  is as in the bulk helium, we obtain the width of a step due to quantum fluctuations:  $\langle u^2 \rangle^{1/2} \sim 0.1a[\ln(l/a)]^{1/2}$ . This estimate illustrates the general theorem: zero oscillations do not destroy an ordering in two dimensions. Recently D. Fisher and Weeks<sup>(10)</sup> have obtained a similar conclusion. However, the problem of the pinning of a step superstructure by the bulk crystal cannot be solved unambiguously by means this theorem. The "pinning-depinning" transition has been considered in the works by Aubry<sup>(11)</sup> and by one of the authors.<sup>(12)</sup> The transition from a locked state of steps to a state with free sliding steps arises at such interstep spacing, that the interaction of the nearest steps becomes equal to the lattice potential. At  $l/a \gg 1$  the interaction depends on  $l$  as

$$(l/a)^{-\Delta-2} = \exp[-(\Delta+2)\ln(l/a)]$$

and the renormalized periodic potential is proportional to

$$\exp\{-\text{const}\langle u^2 \rangle^{1/2}/a\} = \exp\{-\text{const}'[\ln(l/a)]^{1/2}\}$$

if the strains decrease exponentially as  $\exp(-l/l_0)$  far from the step.

More likely a step is smeared out according to the Gauss law  $\sim \exp(-l^2/2l_0^2)$ . In this case the effective periodic potential is of the order of magnitude

$$\exp\left(-\pi \frac{T_\lambda}{\theta_D} \ln \frac{l}{a}\right) \approx \exp\left(-0.3 \ln \frac{l}{a}\right)$$

By virtue of the comparison of this potential with the interaction at typical value  $\Delta = 2$  (see the following section) we conclude that steps are pinned by a crystal lattice at faces with large interstep spacings at least. When  $l$  decreases, there exists a possibility of the transition into an unlocked state of the two-dimensional system of steps. The corresponding areas must be roughened even at zero temperature as it has been suggested by Andreev and Parshin.<sup>(13)</sup>

### 3. SURFACE TENSION AT $T = 0$

The surface tension for the face  $(0, 1, n)$  at  $T = 0$  has been calculated by Landau.<sup>(1)</sup> First we generalize this theory for a more general face  $(0, m, n)$  with  $m \ll n$ . Such faces arise when helium is placed between parallel plates. Two steps with the spacing  $l$  interact according to the powerlike law  $U(l) \sim l^{-\Delta}$ , where  $\Delta = 3$  for van der Waals forces and  $\Delta = 2$  for elastic forces.<sup>(4)</sup>

At zero temperature the problem of the optimal array of steps with the mean spacing  $p = n/m$  on the vicinal face  $(0, m, n)$  can be reduced to the ground state problem for a one-dimensional lattice gas. This problem has been solved in Refs. 13 and 14. The suitable procedure for constructing the ground state structure has been proposed by Hubbard.<sup>(13)</sup> So far as  $p$  is the mean distance between two nearest particles, the distance between a particle and its  $k$ th neighbor can take two different values  $[kp]$  and  $[kp] + 1$  with the probabilities  $r_k = 1 - \{kp\}$  and  $1 - r_k = \{kp\}$ , respectively. Here  $[X](\{X\})$  denotes the integer (fractional) part of  $X$ .

The equilibrium energy of the face  $(0, m, n)$  per a unit length of a step is

$$E(m/n) = \sum_{k=1}^{\infty} (r_k U([kp]) + (1 - r_k) U([kp] + 1)) + \varepsilon_1 \quad (5)$$

where  $\varepsilon_1$  is the energy of a unit length of an isolated step. The function  $E(c)$  can be defined for irrational values  $c$  substituting  $p^{-1}$  by  $c$  in Eq. (5). The

function  $E(c)$  determined in this way is continuous; however, its derivative has jumps at every rational value of  $c$ . This jumps have been calculated in Refs. 15 and 16 and can be written as

$$\Delta \frac{dE}{dc} = \sum_{k=1}^{\infty} (U([kp] - 1) - 2U([kp]) + U([kp] + 1)) \quad (6)$$

As a consequence, the surface tension derivative considered as a function of the slope angle has discontinuities. Equations (5) and (6) can be considerably simplified when  $U(x)$  is a fast decreasing function of  $x$ , e.g.,  $U(x) \sim x^{-k}$  with sufficiently large  $k$ . The right-hand side of Eq. (6) can be estimated as

$$\Delta \frac{dE}{dc} \approx \frac{d^2 U(p)}{dp^2} \quad (6')$$

Henceforth the condition of the fast decrease of  $U(x)$  is assumed to be fulfilled.

The largest discontinuity of the surface tension derivative pointed out in Ref. 1 corresponds to  $c = 0$ , i.e., to the face  $(0, 0, 1)$ . We put it equal to  $2\epsilon_1$ .

There exist two alternative statements of the lattice gas problem. One can fix either the concentration  $c$  or the chemical potential  $\mu = dE/dc$ . In the interface problem the distance from the wall plays a role of the chemical potential. It is worthwhile to declare the results of Refs. 15–17 for a one-dimensional lattice gas with a fixed  $\mu$ .

Every rational value of  $c$  corresponds to a finite segment  $\Delta\mu = \Delta(dE/dc)$  on the  $\mu$  axis given by Eq. (6). The set of these segments densely fills the whole  $\mu$  axis.<sup>(16)</sup> An infinite set of different periodic phases can be described as a branching sequence. It starts with the main sequence of faces  $\langle n \rangle \equiv (0, 1, n)$ . Every bifurcation obeys the rule: between two *neighboring* phases  $\langle A \rangle$  and  $\langle B \rangle$  there appears a dimerized phase  $\langle AB \rangle$ , which is the nearest *neighbor* of the phases  $\langle A \rangle$  and  $\langle B \rangle$  at the next bifurcation.

This possibility was known to I. M. Lifshitz as early as in the Fifties. The bifurcation scheme has first been published in Ref. 2.

In the conclusion of this section let us predict what kind of faces can exist at  $T = 0$  in an experimental sample of finite geometry. We use the fact that the jump  $p^{-1} \Delta\mu(p) \sim p^{-\Delta-3}$  is proportional to the size of a smooth face with the period  $p$  in a crystal shape. By equating this size to the length of an elementary cell  $pa$  we obtain

$$pa \sim Lp^{-\Delta-3}$$

where  $L$  is either the capillar length or the linear size of the interface. In the most favorable case  $L \sim 1$  cm and  $p_{\max}$  cannot exceed  $20 \div 30$  lattice constants.

4. SURFACE ENERGY AND PHASE DIAGRAM AT  $T \neq 0$

At any nonzero temperature the surface energy derivative has a finite number of discontinuities at some rational concentrations  $c$  versus discontinuities at any rational concentration  $c$  at zero temperature. In Fig. 2 the phase diagram for the step system is presented in the  $T-\mu$  plane. In the limit  $T=0$  the bifurcation set described above is reproduced.

Using the transfer-matrix (TM) method to reduce statistical mechanics of steps to quantum mechanics of a one-dimensional lattice gas we construct the phase diagram of Fig. 2. The analogous problem was solved in Ref. 18. So the phase diagram of Fig. 2 is borrowed from it. The most relevant quantity here is the surface energy  $E$  versus the slope angle  $\theta$  of the interface. It should be noted that  $\tan \theta$  coincides with the step concentration  $c$  and is thermodynamically conjugated to the chemical potential  $\mu$ . In the TM method an average direction of steps play the role of the time axis. Along steps there may exist kinks, which correspond to jumps of particles to the neighboring steps of a one-dimensional chain at fixed "time." The jump amplitude coincides with the Boltzmann factor of a kink:  $Z = \exp(-E_0/T)$ .

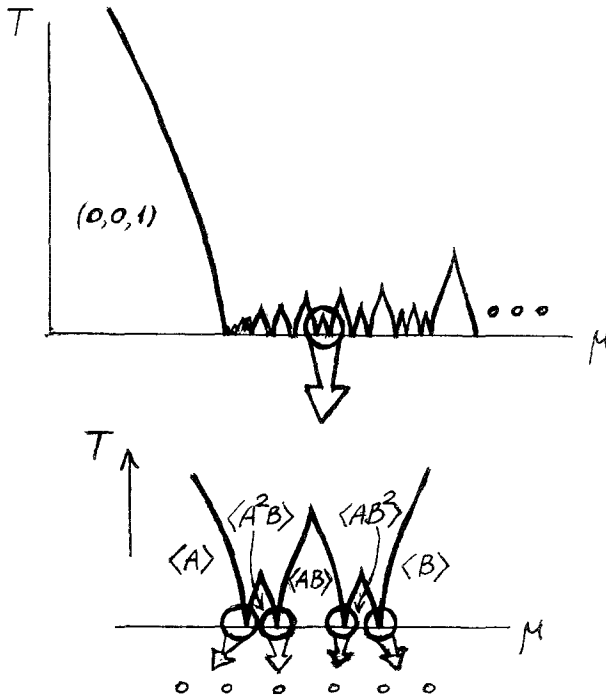


Fig. 2. Phase diagram of a two-dimensional step system. In the bottom of this figure a fine structure of the phase diagram is shown.

Therefore steps can be interpreted as trajectories of particles obeying the Fermi statistics. The free energy of a two-dimensional system of steps corresponds to the ground state energy of the above mentioned one-dimensional chain of fermions.

To demonstrate the applicability of the TM method we calculate the free energy of a face with the step concentration  $c$ , satisfying the inequalities  $n < 1/c < n + 1$ , where  $n$  is an integer. The temperature scale can be divided into three ranges. In its middle part determined by inequalities

$$Z_{\langle n+1 \rangle}^c \gtrsim Z \gtrsim Z_{\langle n, n+1 \rangle}^c \tag{7}$$

only the distances  $n$  and  $n + 1$  between two nearest particles are relevant ( $Z_{\langle A \rangle}^c$  is the critical fugacity of the ordered structure  $\langle A \rangle$ ). Hence, we can introduce a fictitious lattice with sites either occupied with a particle (the distance  $n + 1$  in an initial lattice) or unoccupied (the distance  $n$ ). Only kinks permutating these distances between the nearest steps are taken into account (see Fig. 3). At temperatures defined by inequalities (7) the

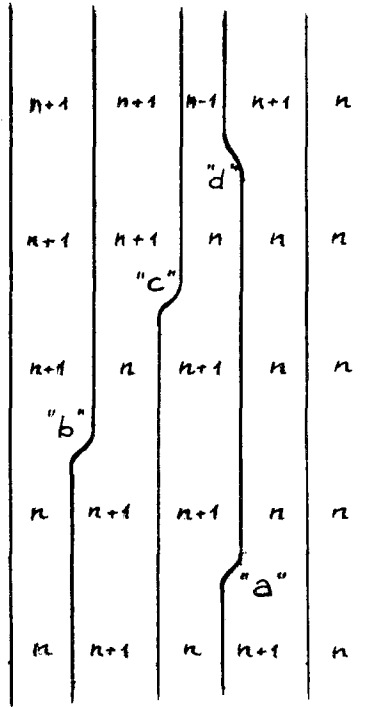


Fig. 3. Possible displacement of steps at the step concentration  $c$  ( $1/(n + 1) \leq c \leq 1/n$ ). The kinks "a", "b," and "c" are allowed for the temperature range, determined by inequalities (7). The kink "d" is not allowed, because one of the distance equal to  $n - 1$  is not conventional.



interaction of fermions is irrelevant. The fermion concentration in the fictitious lattice is equal to  $\{\cot \theta\}$ . The ground state energy of this system per a site of the initial lattice is given by

$$E(c = \tan \theta) = \tan \theta \left( (n+1)U(n) - nU(n+1) + \varepsilon_1 - 2TZ \frac{\sin \pi \{\cot \theta\}}{\pi} \right) \quad (8)$$

In Eq. (8) the  $\theta$ -independent terms are neglected. The last term in Eq. (8) is the energy of the one-dimensional degenerate Fermi gas with the energy spectrum

$$\varepsilon_k = -2TZ \cos k$$

The jump  $\Delta\mu|_{c=1/n}$  is determined from Eq. (8)

$$\Delta\mu(c = 1/n, T) = \Delta\mu(c = 1/n, T = 0) - 4nTZ(T) \quad (9)$$

At the critical temperature  $\Delta\mu$  vanishes. This estimates the smoothing-roughening transition temperature of the face  $(0, 1, n)$  as follows:

$$T_c \exp\left(\frac{-E_0}{T_c}\right) = \frac{1}{4} \frac{d^2U(n)}{dn^2} \quad (10)$$

Previously, transition temperatures of two-dimensional anisotropic systems have been logarithmically estimated by Lyuksyutov *et al.*<sup>(19)</sup> and by Marchenko.<sup>(4)</sup>

Equation (10) provides a good estimate of  $T_c$  but is not rigorous, since near the critical fugacity  $Z_{(n)}^c$ , there is a competition of three allowed distances  $(n-1, n$  and  $n+1)$  instead of the competitions of these distances in separate pairs. A description of this situation by means of a spinless degenerate Fermi gas is insufficient. In Ref. 18 this problem has been reduced to the problem of the planar spin-1 chain which has anisotropy of the "single-ion" type  $(S^Z)^2$  and is placed in a "magnetic field." The equivalence of the phase transitions in the spin-1 chain and in the two-dimensional classical  $XY$  model has been established by Luther and Scalapino<sup>(20)</sup> and by Den-Nijs.<sup>(21)</sup> A discontinuity of  $\mu$  in the vicinity of the transition temperature is

$$\Delta\mu \sim \exp\{-\text{const}/(T_c - T)^{1/2}\} \quad (11)$$

At  $Z > Z_{(n)}^c$ ,  $\mu$  changes continuously, therefore the corresponding region on the interface is roughened.

In the third temperature range  $Z < Z_{(n, n+1)}^c$  the dimerized phase  $\langle n, n+1 \rangle$  with Miller indices  $(0, 2, 2n+1)$  becomes ordered. Like at the

temperature interval (7) spinless fermions can be introduced, but their interaction cannot be neglected. The critical behavior is determined by formulas (4)–(5) of Ref. 18. In our case they look like

$$T_c Z_{\langle n, n+1 \rangle}^c = \frac{1}{2} \left. \frac{d^2 U(p)}{dp^2} \right|_{p=2n+1} \quad (12)$$

$$\Delta\mu = 4\pi(2n+1) \left. \frac{d^2 U}{dp^2} \right|_{p=2n+1} \exp \left\{ \frac{-\pi^2/2 \sqrt{2}}{[(Z_{\langle n, n+1 \rangle}^c - Z)/Z_{\langle n, n+1 \rangle}^c]^{1/2}} \right\} \quad (13)$$

So far we have presented the picture of ordering in the basic sequence of vicinal faces. Its generalization is given below:

On the phase diagram depicted in Fig. 2 the dimerized phase  $\langle AB \rangle$  is created between two neighboring phases  $\langle A \rangle$  and  $\langle B \rangle$ . The estimate of the critical fugacity is  $Z_{\langle AB \rangle}^c \sim 2^{-2-\Delta} \cdot Z_{\langle A \rangle}^c$ . A further temperature decrease leads to an appearance of ordered phases  $\langle A^2 B \rangle$ ,  $\langle AB^2 \rangle$ , etc. The sequence  $\langle A^n B \rangle$  ( $n = 1, 2, \dots$ ) is a specific one. The critical fugacities in this set decrease slowly against the increase of  $n$ , when  $n \gg 1$ . In this case the description of the spin model with a large spin coincides with one of the statistical two-dimensional  $XY$  model. Its critical behavior is known, and singularities have a form of Eq. (11). Any two neighboring phases of the set under consideration, for instance,  $\langle A^n B \rangle$  and  $\langle A^{n+1} B \rangle$ , give rise to a new sequence of ordered phases, beginning from the dimerized phase ( $\langle A^n B A^{n+1} B \rangle$  in the example).

## 5. EQUILIBRIUM SHAPE OF THE INTERFACE

To compare the theoretical predictions with the real experiments it is necessary solve an auxiliary problem for the equilibrium crystal shape in a gravitational field. The first to consider this problem, neglecting the gravitation, has been Wulff.<sup>(22)</sup> He has invented the geometrical method for constructing the surface, using a known form of the surface tension  $\gamma$ . The rigorous proof of Wulff's solution has been presented by Herring.<sup>(23)</sup> An analytic solution of the problem without the field has been derived by Landau<sup>(1)</sup> in the framework of the planar geometry. Recently, Avron *et al.*<sup>(9)</sup> could generalize with the gravitation included Wulff's construction and Landau's analytic solution for a crystal, lying on a horizontal table. Here we consider an interface lying inside a cylindrical volume with arbitrarily shaped normal section (Fig. 4). The cylindrical axis is assumed to be horizontal. We also assume that the crystal axis, which is perpendicular to the crystal face  $(0, 0, 1)$ , lies in the plane of the normal section. These conditions lead to the plane geometry, i.e., vicinal faces are of the type

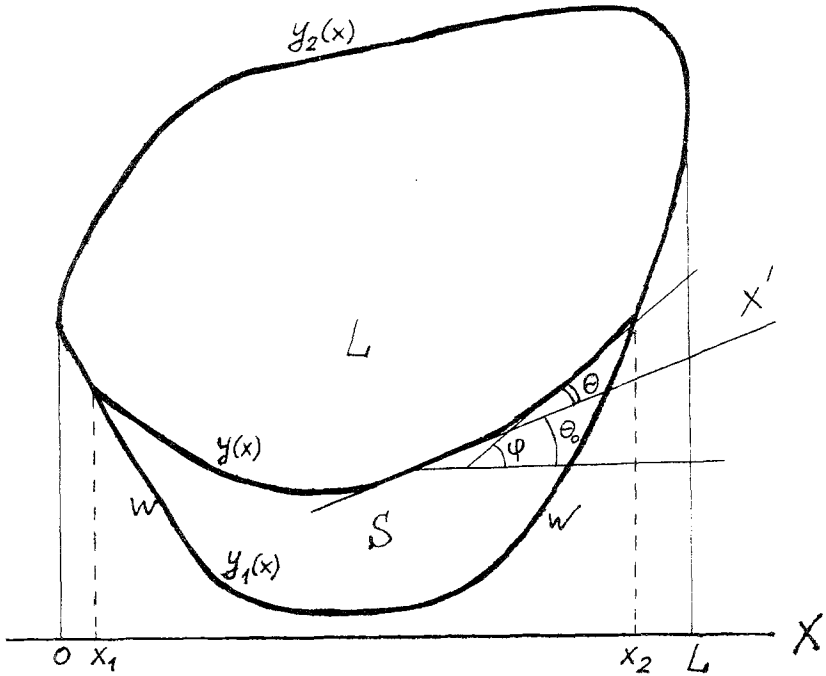


Fig. 4. Normal section of a cylindrical volume, containing the interface  $y(x)$ . The bottom part of this volume corresponds to the curve  $y_1(x)$ , the top part corresponds to  $y_2(x)$ .

(0,  $m$ ,  $n$ ), and the surface tension  $\gamma$  depends on the angle  $\theta$  only (see Fig. 4). Since optical measurements so far are the main source of information about the crystal shape assumed to be homogeneous along the ray direction (see, for instance, Ref. 5), our assumptions hold.

To solve this auxiliary problem we must minimize the functional

$$\begin{aligned} \mathcal{F} = & \int_{x_1}^{x_2} \gamma_{SL}(\theta) dl + \int_{x_1}^{x_2} \gamma_{SW} dl_1 + \left( \int_0^{x_1} + \int_{x_2}^L \right) \gamma_{LW} dl_1 \\ & + \frac{1}{2} \rho_L g \int_0^L (y_2^2 - y_1^2) dx + \frac{1}{2} (\rho_S - \rho_L) g \int_{x_1}^{x_2} (y^2 - y_1^2) dx \end{aligned} \tag{14}$$

with the constraint

$$\int_{x_1}^{x_2} (y(x) - y_1(x)) dx = V_S \tag{15}$$

Equation (15) implies that the volumes of the liquid and solid phases are constant at the equilibrium crystallization. All the types of the surface

tensions are taken into account in the first three terms of the functional  $F$ :  $\gamma_{SL}$ ,  $\gamma_{SW}$ , and  $\gamma_{LW}$  are tensions on the boundaries "solid-liquid", "solid-wall," and "liquid-wall," respectively. We integrate over the interface  $y(x)$  in the first term and over the external surface  $y_1(x)$  in the other two terms. The remaining terms on the right-hand side of Eq. (14) denote the gravitational energy of the two-component system.

In the preceding sections we have calculated the energy  $E(c)$  of a step system per unit area of the face  $(0, 0, 1)$ . In Fig. 4 the trace of this plane coincides with the axis  $X'$ , rotated by the angle  $\theta_0$  from the horizontal axis  $X$ . Hereafter we shall use a surface tension  $\gamma$  and a surface energy  $\alpha$  per a unit horizontal area. Those both energies can be expressed via the energy  $E(c)$  by means of the following equalities:

$$\gamma = \frac{E(\theta)}{\cos \theta} = \frac{\alpha(\varphi)}{\cos \varphi} \quad (16)$$

The angles  $\theta$  and  $\varphi$  in Fig. 4 are related by the obvious equation:  $\varphi = \theta + \theta_0$ . It is noteworthy that  $dy/dx = \tan \varphi$ .

The Euler equations and boundary conditions for the edge angles are

$$p \frac{d^2 \alpha}{dp^2} dp = (Gy + \lambda) dy \quad (17)$$

$$\frac{d^2 \alpha}{dp^2} dp = (Gy + \lambda) dx$$

$$\left[ \frac{d\alpha}{dp} p_1 + \alpha - \Delta\gamma (1 + p^2)^{1/2} \right]_{x=x_1(x_2)} = 0 \quad (18)$$

where  $G = g(\rho_s - \rho_l)$ ,  $\Delta\gamma = \gamma_{LW} - \gamma_{SW}$ ,  $p = dy/dx$ ,  $p_1 = dy_1/dx$ .

The edge angles  $\varphi_+$  and  $\varphi_-$  are determined by two Eqs. (18). It should be emphasized that Eqs. (18) also describe the case of the "liquid-liquid" interface, when  $\gamma_{LL}$  is not  $\varphi$  dependent.

In the case of an asymmetric crystal growth ( $\theta_0 \neq 0$ ) the edge angles differ by their absolute values even at a symmetric volume geometry. The function  $d\alpha/dp$  has jumps for each rational  $\tan \theta$  at zero temperature. Hence, a plane strip on the interface, corresponding to the integer Miller indices, is fixed in a closest vicinity of the external (wall) boundary. At  $T \neq 0$  the function  $d\alpha/dp$  has a finite number of jumps (cf. Section 4), so near the external boundary both smooth and rough areas of the interface can exist. This behavior is qualitatively illustrated by Fig. 5.

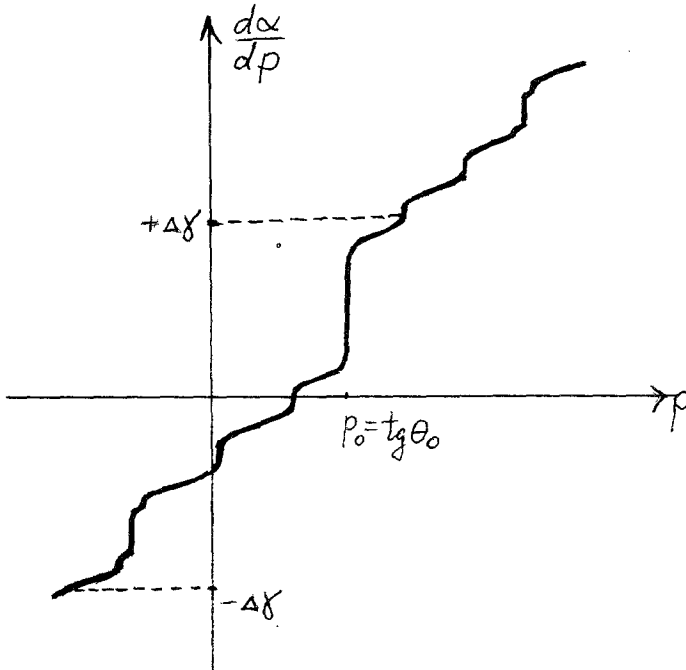


Fig. 5. Graph solution of Eq. (18) is shown for the case of vertical walls. The asymmetry of function  $d\alpha/dp$  is due to nonzero  $\theta_0$ .

The solution of the Euler Eqs. (17) can be expressed parametrically:

$$G_y + \lambda = R(p)$$

$$x = x_0 + \int_0^p \frac{d^2\alpha}{dp^2} \frac{dp}{R(p)} \tag{19}$$

where  $R = ((Gy_0 + \lambda)^2 + 2G\{p(d\alpha/dp) - [\alpha(p) - \alpha(0)]\})^{1/2}$ , and  $(x_0, y_0)$  is the interface coordinates corresponding to  $p = 0$ . The Lagrange factor  $\lambda$  can be interpreted as pressure. One finds a simple formula for it in the case of vertical walls. The integration of the second Eq. (17) leads to the relation

$$\lambda = \Delta\gamma/L \tag{20}$$

The sizes of plane strips on the interface are

$$\Delta x = \Delta \frac{d\alpha}{dp} / R \tag{21}$$

To estimate these sizes we use the average form of the surface energy:

$$E = \varepsilon_0 + \varepsilon_1 \tan \theta + \varepsilon_2 (\tan \theta)^\Delta$$

Here  $\varepsilon_0$  is the energy of interface creation,  $\varepsilon_1$  is the energy of step creation on the face (0, 0, 1), the last term describes the interaction of steps. To observe the ordering on the vicinal faces most favorably, the plane strip of the face (0, 0, 1) must be located at least at distances of the order of  $\sim 1$  mm (capillar length) from the wall. By virtue of this condition vicinal faces occupy large summary area, corresponding approximately to a real interface length  $\sim 1$  cm. This holds if  $(\Delta\gamma)^2 \sim GL^2\gamma_{SL}p_0^\Delta$ , as the analysis of Eq. (19) reveals.

## 6. SUMMARY

Here we summarize those conclusions of our theory which can be tested experimentally. It is shown that the faces being vicinal to the stable face are also stable at sufficiently low temperatures. The ordering temperatures of faces which are vicinal to the face (0, 0, 1) can be estimated as  $T_c(n) \sim T_0/\ln n$ , where  $n$  is a period of a step structure on a vicinal face;  $T_0$  is the ordering temperature of the face with the interstep spacing of the order of an interatomic spacing. Recently, Wolf *et al.*<sup>(8)</sup> have observed the 60° face on the <sup>4</sup>He crystal shape with the ordering temperature 0.36 K. This value can be suggested as a  $T_0$  candidate. Therefore we have an estimate  $T_c(n) \lesssim 0.1$  K.

The critical behavior of any plane strip size is universal and described by Eq. (11). The confirmation of this law by optical measurements is inadequate, because the optical resolution limit  $\sim 1 \mu\text{m}$ . At zero temperature the linear size of an ordered face cannot exceed  $\sim 1$  mm, so the above-mentioned law is experimentally violated at  $(T_c - T)/T_c \sim 1/50$ .

It would be extremely interesting to find the step structure on the interface by diffraction methods. So far we can suggest only one possibility, associated with the use of hypersound.

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