

Cylindrical faceting of crystals in equilibrium with a moving superfluid liquid

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General relations for surface thermodynamic functions characterizing the interface between a helium crystal and a moving superfluid liquid are developed. It is shown that atomically smooth crystal facets in the presence of motion are unstable to the formation of pairs of steps perpendicular to the liquid velocity. Equilibrium crystal faceting at low temperatures is cylindrical in character. The facet shape and the angular dependence of the crystal surface stiffness are found. © 1994 American Institute of Physics.

Helium crystals at low temperatures may be in thermodynamic equilibrium with a superfluid liquid moving parallel to the crystal surface. As is shown below, the relative motion of the liquid and the crystal modifies the thermodynamic characteristics and structure of the equilibrium crystal surface. The contribution of the motion to the surface energy or, in other words, the surface part of the kinetic energy of the system, is completely determined by specifying the two-dimensional tensor of the surface normal component density. This quantity, as a characteristic of the superfluid liquid-solid interface, was introduced earlier¹ and calculated for a randomly rough surface.

In the present work, the surface normal density is found for crystal surfaces differing from the atomically smooth basis facet in having a small concentration of steps on them. The singularity in the concentration dependence of the surface normal density turns out to be so strong that, for an arbitrarily low liquid velocity, the atomically smooth facet is unstable with respect to the spontaneous formation of pairs of steps perpendicular to the relative liquid velocity. The physical reason for the instability is the large negative kinetic energy of a single step of perpendicular orientation. At the same time, the energy of the steps directed parallel to the velocity is positive and equals its stationary value. A direct consequence of this instability is that low-temperature crystal faceting must have a very unusual character. The intersection of the crystal surface and a plane parallel to the velocity is a regular curve having no rectilinear portions. Below we find the actual form of such a curve and the corresponding angular dependence of the crystal surface stiffness. At the same time, the intersection with a plane perpendicular to the velocity has the same form as for no motion, i.e., it does contain a straight portion at low temperatures.

Thus, the faceting of a crystal in equilibrium with a moving superfluid liquid becomes cylindrical in character. It is interesting to note that this type of faceting was treated earlier² thermodynamically for low-symmetry facets, which is what any facet becomes if there is a preferred direction of the relative liquid velocity.

It should be emphasized that in the general case the dependence of the kinetic energy of a crystal-liquid flow system on the shape of the crystal is a bulk effect. The surface

kinetic energy contributes little to the shape-dependent part of the total kinetic energy. However, in our case, which is concerned with surface structure changes (the appearance of a stepped superstructure) near certain special orientations, with no marked changes in the global macroscopic crystal shape, it is precisely the surface kinetic energy which plays the dominant role. In a similar way, the effect of liquid motion on other, say strictional, surface structures²⁻⁵ may be described.

1. GENERAL THERMODYNAMIC RELATIONS

Consider the helium crystal–superfluid interface at low temperatures, when the bulk normal component may be neglected. In thermodynamic equilibrium the difference between the crystal velocity \mathbf{v}_c and the superfluid velocity \mathbf{v}_l is parallel to the interface. The phase boundary can always be chosen so that there is no surface mass.^{6,7} The surface momentum \mathbf{p}_s , which is also parallel to the interface, is then invariant under a Galilean transformation. The surface normal density $\nu_{\alpha\beta}$ is defined¹ as the coefficient of proportionality between the Galilean invariants \mathbf{p}_s and $\mathbf{v}_c - \mathbf{v}_l$:

$$p_{s\alpha} = \nu_{\alpha\beta} (\mathbf{v}_c - \mathbf{v}_l)_\beta, \quad (1)$$

where the indices α and β may assume two values in the interface plane.

For $\mathbf{p}_s \neq 0$, the energy per unit area of the surface, α , is not Galilean-invariant. Its value $\alpha(\mathbf{v}_c, \mathbf{v}_l)$ in an arbitrary reference frame relates to its value α_l in the frame fixed in the liquid by the Galilean transformation

$$\alpha(\mathbf{v}_c, \mathbf{v}_l) = \mathbf{p}_s \mathbf{v}_l + \alpha_l(\mathbf{p}_s), \quad (2)$$

and α_l considered as a function of the surface momentum \mathbf{p}_s satisfies the thermodynamic identity

$$d\alpha_l = (\mathbf{v}_c - \mathbf{v}_l) d\mathbf{p}_s, \quad (3)$$

which implies the symmetry of the tensor $\nu_{\alpha\beta}$.

In view of Eqs. (1) and (3), for low velocities,

$$\alpha_l = \alpha_0 + \frac{1}{2} \nu_{\alpha\beta} v_\alpha v_\beta, \quad (4)$$

where $\mathbf{v} = \mathbf{v}_c - \mathbf{v}_l$ and α_0 is the surface energy at $\mathbf{v}_l = \mathbf{v}_c = 0$.

By substituting (4) into (2) we find the surface part $\alpha - \alpha_0$ of the kinetic energy of the system:

$$\alpha(\mathbf{v}_c, \mathbf{v}_e) - \alpha_0 = \frac{1}{2} \nu_{\alpha\beta} (v_{c\alpha} v_{c\beta} - v_{l\alpha} v_{l\beta}). \quad (5)$$

In the general case the tensor components $\nu_{\alpha\beta}$ need not satisfy any thermodynamic inequalities. So the only conclusion to draw from Eq. (5) is that if in the rest frame of the liquid ($\mathbf{v}_l = 0$) the surface kinetic energy $\alpha - \alpha_0$ is positive, then in the crystal rest frame ($\mathbf{v}_c = 0$) it is negative, and vice versa.

If a crystal at rest ($\mathbf{v}_c = 0$) is in liquid flow $\mathbf{v}_l \neq 0$, the equilibrium structure at each point of the surface should satisfy the condition that the local surface energy

$$\alpha_c = \alpha_0 - \frac{1}{2} \nu_{\alpha\beta} v_{\alpha} v_{\beta} \quad (6)$$

be minimized for a given $\mathbf{v} = -\mathbf{v}_l, \mathbf{v}_l$ being the local value of the tangential velocity of the liquid. It is important to emphasize (see above) that the surface structure changes we are discussing must not be accompanied by any substantial changes in the global macroscopic shape of the crystal.

As the surface structure is clearly unchanged by the Galilean transformation, in an arbitrary reference frame the expression

$$\alpha_c = \alpha_0 - \frac{1}{2} \nu_{\alpha\beta} (\mathbf{v}_c - \mathbf{v}_l)_\alpha (\mathbf{v}_c - \mathbf{v}_l)_\beta, \quad (7)$$

should be a minimum, where \mathbf{v}_c is the crystal velocity and \mathbf{v}_l is the local liquid velocity.

It is of interest to explore the condition that (7) be a minimum for a crystal of finite size moving as a whole with velocity \mathbf{v}_c in an unbounded liquid in a reference frame in which the liquid velocity vanishes at infinity. In this frame, the system is characterized by an energy spectrum $E = E(\mathbf{P})$, where E and \mathbf{P} are the total energy and total momentum and $dE = \mathbf{v}_c d\mathbf{P}$ (see Ref. 8). The thermodynamically stable states correspond to an energy spectrum satisfying the condition that the energy be minimal for a given value of the momentum. By applying the Legendre transformation

$$E' = E - \mathbf{v}_c \mathbf{P}, \quad (8)$$

$$dE' = -\mathbf{P} d\mathbf{v}_c, \quad (9)$$

we find the thermodynamic potential E' , which in view of Eq. (9) is a minimum at a given velocity \mathbf{v}_c . Our case, then, implies the minimization of the local values E'_s of the surface part of the potential E'

$$E'_s = E_s - \mathbf{v}_c \mathbf{p}_s, \quad (10)$$

where $E_s = \alpha(\mathbf{v}_c, \mathbf{v}_l)$ and \mathbf{p}_s are the local values of the surface parts of the energy E and the momentum \mathbf{P} . By substituting (1) and (5) into (10) we obtain an expression identical to Eq. (7): $E'_s = \alpha_c$.

The sign of the surface kinetic energy can be specified in the case (of importance here) in which the dominant role is played by a surface superstructure having a period much larger than the crystal lattice period. Suppose a crystal, the macroscopically flat surface of which has such a superstructure, moves parallel to its surface in a liquid which is at rest at infinity. The presence of a moving superstructure generates a motion in the liquid which propagates into the liquid a

distance on the order of the structure period. Macroscopically (i.e., when all quantities are averaged over regions much larger than the structure period), the kinetic energy of this motion is the total surface part of the kinetic energy of the system in the present case. It is positive and hence the surface under study is characterized by a surface normal density $\nu_{\alpha\beta}$ satisfying the condition that the quadratic form $\nu_{\alpha\beta} v_{\alpha} v_{\beta} > 0$ be positive definite. According to Eq. (6), the surface kinetic energy $\alpha_c - \alpha_0$ in the crystal rest reference frame is then negative. Since it is precisely α_c which possesses the minimal property at a given velocity, this clearly implies that the motion of the liquid favors the formation of superstructures and generally of any types of macroscopic roughnesses at the surface.

2. BASIS FACET STRUCTURE

Suppose that on the initial, atomically smooth basis facet a superstructure represented by a system of parallel steps forms. For the overall surface orientation to conserve, the average concentrations of the positive and negative steps must be equal. Suppose also that the total step concentration $c = na$, where n is the total number of steps per unit length and a the lattice period, is small compared to unity. In the absence of motion the surface energy α_0 per unit area is

$$\alpha_0 = \alpha_0^{(0)} + c\beta,$$

where $\alpha_0^{(0)}$ is the surface energy of the initial smooth facet and βa is the energy per unit step length.

Let the crystal move with velocity \mathbf{v} parallel to the flat mid-surface and let the liquid at infinity be at rest. The problem of calculating the kinetic energy of the motion generated in the liquid by a stepped-surface crystal moving in it is analogous to the A. Kosevich–Yu. Kosevich⁹ problem concerning the kinetic energy of the steps involved in the crystal growth process. At distances r from the axis (identical with the step) such that $a \ll r \ll a/c$, a moving step generates an axisymmetric motion in the liquid with velocity $v_l(r)$ directed either away from the step axis or toward it, depending on the sign of the step. Assuming the velocity \mathbf{v} to be small compared to the sound speed, the liquid can be considered incompressible. From the incompressibility condition we find

$$\pi r v_l(r) = \pm a v_x,$$

where v_x is the projection of the crystal velocity on the x -direction perpendicular to the step direction, so that

$$v_l(r) = \pm \frac{a v_x}{\pi r}.$$

The kinetic energy of the liquid motion resulting from the motion of a single step is

$$\frac{\rho}{2} \int v_l^2(r) \pi r dr = \frac{\rho a^2}{2\pi} v_x^2 \ln \frac{c_0}{c},$$

where c_0 is a constant of order unity and ρ is the liquid density, and where the logarithmic integral is cut off at the

lower limit at $r \sim a$ and at the upper at $r \sim a/c$. From this the surface energy in the liquid rest reference frame is found to be

$$\alpha_l = \alpha_l^{(0)} + c\beta + c \frac{\rho a}{2\pi} v_x^2 \ln \frac{c_0}{c},$$

corresponding to a single nonzero component in the difference $\nu_{\alpha\beta}(c) - \nu_{\alpha\beta}(0)$:

$$\nu_{xx}(c) - \nu_{xx}(0) = \frac{\rho a}{\pi} c \ln \frac{c_0}{c}. \quad (11)$$

According to Eqs. (7) and (11), the surface energy in the crystal-fixed frame, which must be a minimum at a given velocity \mathbf{v} , has the following form:

$$\alpha_c = \alpha_c^{(0)} + c\beta - c \frac{\rho a}{2\pi} v_x^2 \ln \frac{c_0}{c}. \quad (12)$$

From the minimization condition for (12) we find that the steps must be arranged perpendicular to the velocity \mathbf{v} and that their equilibrium concentration

$$c \sim \exp\left(-\frac{2\pi\beta}{\rho a v^2}\right) \quad (13)$$

is exponentially small at small velocities.

For given positive- and negative-step concentrations, the structures may vary as to the alternation and arrangement of the steps. We shall not be concerned here with the problem of determining the structure in full. Let us only note the following. No periodic structure can be in equilibrium. In fact, a surface with a periodic structure of steps has a finite width l , which may be defined by

$$l^2 = \lim_{|r| \rightarrow \infty} K(x, y),$$

where $\mathbf{r} = (x, y)$ is the two-dimensional radius vector in the surface,

$$K(x, y) = \langle [z(\mathbf{r}) - z(0)]^2 \rangle \quad (14)$$

is the correlation function, and $z = z(\mathbf{r})$ is the equation of the surface. The average in Eq. (14) is an ordinary statistical average. For any surface of finite width one can introduce a notion of a "second-generation" step whose energy is finite and which corresponds to a displacement of the surface and the superstructure as a whole by one lattice period (see Refs. 10, 11). For a surface containing second-generation steps with concentration c , a formula analogous to Eq. (12) holds, which shows clearly the instability of the periodic structures. One can therefore argue that as a result of the evolution of the instability of an atomically smooth facet we are discussing, a nonperiodic structure of steps must arise, for which it is impossible to introduce the notion of a step perpendicular to the velocity. The equilibrium surface should therefore exhibit unusual properties. Namely, the effective surface width l_x longitudinal with respect to the velocity is infinite,

$$l_x^2 = \lim_{|x| \rightarrow \infty} K(x, 0) = \infty$$

(even at zero temperature). The surface is atomically rough in the longitudinal direction. At the same time the transverse width

$$l_y^2 = \lim_{|y| \rightarrow \infty} K(0, y) < \infty$$

is finite (at least at zero temperature. At finite temperature, the faceting may be destroyed by local topological excitations of the dislocation-loop type, see Ref. 12). The surface is atomically smooth in the transverse direction.

The basis facet properties we have formulated correspond to the cylindrical crystal faceting previously considered² for low symmetry facets. The cylindrical faceting is the appearance at the crystal surface of singular portions, of finite size, one of whose two principal radii of curvature is infinite (in our case, this is the radius of curvature of the curve obtained by cutting the surface with the plane perpendicular to the velocity). It may also be said that the equilibrium basis facet is characterized by effective steps longitudinal with respect to the velocity having finite energy, and transverse effective steps with zero energy.

3. SURFACE STIFFNESS

The above results enable one to predict the equilibrium crystal shape near the point where the basis facet appears at the crystal surface, and to determine the thermodynamic functions of the vicinal facets. Since the surface is cylindrical, it is of particular interest to find the form of the cylinder generatrix, i.e., of the curve which is obtained when the crystal surface is cut by the xz plane passing through the surface normal at the point where the basis facet emerges (z axis), and through the velocity vector \mathbf{v} (x axis). Let $h \equiv dz/dx = \tan \theta$, where $z = z(x)$ is the equation of the required curve and θ the angle between the surface normal at point x and the z axis. It will be assumed that $\theta > 0$ ($h > 0$) and $x > 0$. The shape of the surface $z = z(x)$ for $x < 0$, and its properties for $\theta < 0$ ($h < 0$), are determined easily by using the symmetry of the problem under the transformation $x \rightarrow -x$; this symmetry implying, for example, that $z(-x) = z(x)$.

For the vicinal facets the angle θ is small. The surface thermodynamic functions are calculated easily by assuming that, apart from the condition $\theta \ll 1$, the angle θ also obeys $\theta \gg c$, where c is the equilibrium step concentration at the basis facet, Eq. (13). The concentration h of the steps of one sign which are necessary for the overall orientation to change by an angle θ with respect to the basis facet is then large compared to the concentration of the steps of the opposite sign, so these latter may be neglected. The (incompletely known) structure of the equilibrium basis facet is not important for $\theta \gg c$. According to Eq. (12), the contribution $\Delta \alpha_c$ of the kinetic energy of the steps to the surface energy α_c is

$$\Delta \alpha_c = -\frac{\rho a}{2\pi} v^2 h \ln \frac{c_0}{h}. \quad (15)$$

For future convenience, we introduce instead of $\alpha_c(\theta)$ the function

$$f(h) = \sqrt{1 + h^2} \alpha_c(\theta). \quad (16)$$

The surface stiffness $\tilde{\alpha}(\theta)$ for small θ may be defined by the two equivalent expressions

$$\tilde{\alpha} = \alpha_c(\theta) + \frac{\partial^2 \alpha_c}{\partial \theta^2}, \quad \tilde{\alpha} = \partial^2 f / \partial h^2. \quad (17)$$

In the absence of liquid motion ($\mathbf{v}=0$), the surface stiffness of the vicinal facets is due to the long-range step-step interaction and vanishes linearly as $h \rightarrow 0$: $\tilde{\alpha}(h) = 2\gamma h$ (see Ref. 11, p. 47), where γ is a positive interaction constant. By adding the second derivative of (15) it is found that

$$\tilde{\alpha}(h) = 2\gamma h + \frac{\rho a}{2\pi h} v^2. \quad (18)$$

The motion of the liquid with velocity \mathbf{v} thus has the consequence that as the angle θ is decreased the surface stiffness $\tilde{\alpha}(\theta)$ first decreases linearly, then reaches the minimum value

$$\tilde{\alpha}_{\min} = 2v(\rho\gamma a/\pi)^{1/2}$$

at $\theta = v(\rho a/4\pi\gamma)^{1/2}$, and finally increases inversely as θ . At the boundary $h \sim c$ of the region of applicability of Eq. (18), the surface stiffness reaches the exponentially large maximum value

$$\tilde{\alpha}_{\max} \sim \rho a v^2 \exp\left(\frac{2\pi\beta}{\rho a v^2}\right).$$

It would be interesting to observe the surface stiffness features discussed above by applying the method of Ref. 13 using the experimental angular dependence of the crystallization wave spectrum.

4. EQUILIBRIUM SURFACE SHAPE

Integrating Eq. (18) twice and using the second of Eqs. (17) we find the surface thermodynamic potential $f(h)$ of the vicinal faces,

$$f(h) = \alpha_0 + \beta h + \frac{1}{3} \gamma h^3 - \frac{\rho a}{2\pi} v^2 h \ln \frac{c_0}{h}. \quad (19)$$

Here α_0 and β are the constants of integration. The former is obviously the surface energy of the initial atomically smooth face, and the latter the step energy at this face (divided by the lattice period a).

In order to find an equilibrium curve equation $z = z(x)$ corresponding to the expression (19) for the surface potential $f(h)$, it is convenient² to introduce, instead of h , the new variable

$$\eta = \frac{\partial f}{\partial h} = \beta + \gamma h^2 - \frac{\rho a}{2\pi} v^2 \ln \frac{c_0}{eh} \quad (20)$$

and to apply the Legendre transformation by introducing a new potential

$$\tilde{f} = f - \eta h = \alpha_0 - \frac{2}{3} \gamma h^3 - \frac{\rho a}{2\pi} v^2 h. \quad (21)$$

To within the normalization of the variables, the potential $\tilde{f} = \tilde{f}(\eta)$ viewed as a function of the variable η is the same function as $z = z(x)$. Namely,

$$-\frac{z(x)}{\lambda} = \tilde{f}(\eta), \quad \eta = \frac{x}{\lambda}, \quad (22)$$

where λ is a scaling normalization factor determined by the specific value of the crystal volume.

Equations (20) and (21) represent a parametric definition, with h the parameter, of the function $\tilde{f} = \tilde{f}(\eta)$. The condition for their applicability is given by the inequalities $1 \gg h \gg c$, where c is the basis facet step concentration. Using Eq. (22) we find the parametric equation for the curve $z = z(x)$

$$x = 1 + gh^2 - x_0 \ln \frac{c_0}{eh}, \quad z = \frac{2}{3} gh^3 + x_0 h, \quad (23)$$

where $g = \gamma/\beta$ and $x_0 = (\rho a/2\pi\beta)v^2$ are dimensionless parameters and $x_0 \ll 1$. In Eqs. (23) the scaling factor is chosen to be $1/\beta$, which corresponds to taking for the unit of length the quantity $\lambda\beta$, the size of the flat portion of the basis facet in the absence of motion ($v=0$). It is also assumed that the z axis points into the crystal and that the origin of the z coordinate coincides with the point where the basis facet appears at the surface, and thus corresponds to the condition $z=0$ for $h=0$.

On its small- x side the region of applicability of Eqs. (23) is bounded by the condition $x \gg x_0$, which corresponds to the condition $h \gg c$ above. For $x \lesssim x_0$, the specific structure of the system of steps on the basis facet becomes important. The upper boundary of the region of applicability of Eqs. (23) lies at $x > 1$ and corresponds to the inequality $x - 1 \ll 1$, which is equivalent to $h \ll 1$.

If $x \gg x_0$ holds, while we have $x < 1$ and $1 - x \gg x_0$, then from Eq. (23) we find the simple equation

$$z(x) = cx_0 e^{x/x_0}.$$

For $x > 1$, but $1 \gg x - 1 \gg x_0$, we obtain

$$z(x) = \frac{2}{3} g^{-1/2} (x-1)^{3/2},$$

which corresponds to the known (see Ref. 11, p. 58) crystal shape behavior in the absence of liquid motion near the boundary of the flat portion.

In conclusion, the motion of the liquid results in the destruction of the atomically smooth state of the surface in the transverse (relative to the velocity) direction as well as modifying the character of the angular dependence of the surface stiffness. Instead of $\tilde{\alpha} \propto h$, for h sufficiently small Eq. (18) suggests $\tilde{\alpha} \propto h^{-1}$. On the other hand, the motion has an orienting effect on those steps already in existence, by aligning them perpendicular to the velocity. If in the absence of motion the surface was atomically rough and its step concentration low, then the motion is expected to make the surface atomically smooth in the direction perpendicular to the velocity, thus leading to $\tilde{\alpha} \propto h_{\perp}$. In the longitudinal direction, the law $\tilde{\alpha} \propto h_{\parallel}^{-1}$ mentioned above may operate. The features discussed may be of significance in processing experiments^{13,14} on the angular dependence of stiffness, in which motion of the liquid due to heat flow is possible.

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