Crystal Shape near the Faceting Phase Transition Point

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The critical behavior of an equilibrium shape of a crystal with the size much larger than the capillary length is studied near the faceting phase transition point.

1. INTRODUCTION

Faceting phase transitions have recently attracted special attention in view of studying surface properties of solid helium. Contrary to ordinary crystals, in solid helium quantum processes of particle tunneling[1] are of major significance, so that an equilibrium crystal shape sets in for anomalously small times[2,3]. On the other hand, faceting phase transitions have been observed in solid helium.[4,5,3] Although the concept of such transitions was introduced by Burton, Cabrera, and Frank[6,7] many years ago, they were observed in ordinary crystals only qualitatively, the major difficulty being caused by enormous equilibrium-shape establishment times. In helium crystals this difficulty is lifted, so there arises a unique opportunity for experimentally studying the thermodynamics of such transitions, which is common for classical and quantum crystals.

Faceting is a phase transition between two different states of a surface—atomically rough and atomically smooth. It is therefore obvious that the problem of establishing the nature of a phase transition depends on the choice of a particular order parameter characterizing this transition. There are two approaches to the problem. The first one[8,9] is based on the

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definition according to which the surface is smooth or rough, depending on whether the mean-square amplitude of surface fluctuations about the equilibrium position is finite or infinite (in the thermodynamic limit in the absence of gravity). The second approach is directly related to studying the surface energy as a function of surface orientation.[10] In this case, the surface is assumed to be rough or smooth, depending on whether the function describing the angular dependence of the surface energy is analytic or has a cusp. Although at finite temperatures any surface with analytic surface energy is characterized by infinite (in the above sense) fluctuations, these two definitions are by no means equivalent, the difference being most striking at zero temperature. As was shown in Ref. 2, quantum delocalization of steps on the surface may lead (and for high-index surfaces does lead) to the fact that the crystal surface is characterized by an analytic surface energy even at zero temperature, while the first criterion[8,9] implies that any surface is smooth at zero temperature. It should be stressed here that the free surface of liquid helium at zero temperature is smooth in the sense of the first definition, but rough in the sense of the second definition. As was noted above, at finite temperatures both definitions coincide. However, from the point of view of the second approach the divergence of the fluctuation displacement is a secondary effect, rather than the primary one. Let us elucidate the situation, using an analogy with the case of proper and improper ferroelectrics known in the theory of ordinary secind-order phase transitions. In proper ferroelectrics spontaneous polarization is an order parameter responsible for the phase transition. In improper ferroelectrics, the order parameter has another origin, and the phase transition is accompanied with the onset of spontaneous polarization as a secondary effect. It is known[11] that the thermodynamics of the phase transition is quite distinct in these two cases.

The previous thermodynamic mean-field theory of faceting phase transitions[10] predicts an equilibrium shape near the phase transition point only for sufficiently small crystals, much smaller than the capillary constant (about 1 mm for solid helium). Experimental results obtained by Keshishev, Parshin, and Babkin[3] (see also Ref. 12) agree qualitatively with the theory. Quantitative comparison is difficult because experiments are usually performed with bulk samples, for which gravity and interaction of the surface with vessel walls become significant. In the present paper the results of Ref. 10 are extended to this case, and it is shown that in most important situations, near the phase transition point, the shape of the surface (over the main are) virtually does not depend on the character of interaction with the walls, but strongly depends on the vessel size. This interesting circumstance is very significant from an experimental point of view.

2. TEMPERATURE DEPENDENCE OF THE FACET SIZE

The problem of calculating the shape of a crystal near the faceting phase transition point is usually stated as follows. Suppose the space between the waals of a vessel formed by two parallel vertical planes separated by a distance of $2L$ is filled with a crystal (in the lower part) and a liquid, which is in equilibrium with the crystal. At a temperature T, below the transition point T_c, the interface has a flat part (Fig. 1a) whose length 21 depends on temperature and vanishes at $T = T_c$. For $T > T_c$ (Fig. 1b) the interface does not have singularities. What we need is to derive an equation $z = z(x)$ of the equilibrium interface, where the axis z is vertical and the axis x is normal to the walls.

In a general case, the situation depends, naturally, on the crystal lattice orientation relative to the walls. Below we shall consider the most symmetric configurations, which are important from the experimental point of view. Of most interest in ^{4}He crystals are faceting phase transitions on the basal plane perpendicular to the six-fold symmetry axis, and also those on the faces normal to the two-fold symmetry axis and to two symmetry planes. These transitions can easily be observed experimentally. In ^{3}He crystals faceting transitions have not so far been observed, but, if there be any, they are most likely to occur on the basal faces normal to the four-fold symmetry axis and to two symmetry planes. We shall perform calculations precisely for these cases, assuming the crystal to be so oriented that its symmetry axis is vertical. Furthermore, we shall assume that in the case of the four-fold symmetry axis one of the symmetry planes is parallel to the walls. According
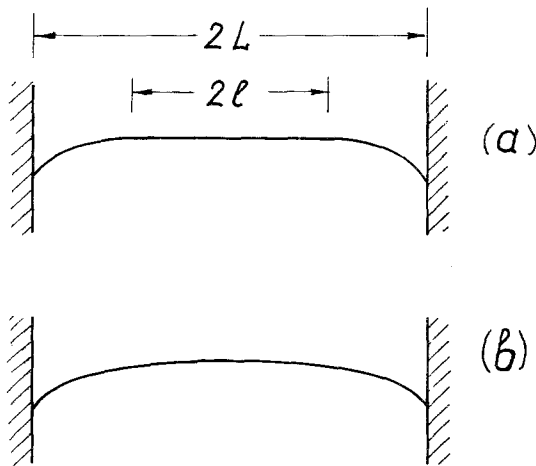

Fig. 1.   Crystal shape. (a) Below the transition point. (b) Above the transition point.

to Ref. 10, if a faceting phase transition takes place on the face normal to the two-fold symmetry axis, the surface is flat along one direction only (we shall assume that this direction is perpendicular to the walls). In all the cases discussed here the shape of the surface is such that the function $z(x)$ can be considered symmetric, i.e., $z(x) = z(-x)$.

For $T < T_c$ the total surface free energy per unit length along the y axis is

$$\mathcal{F} = 2f(0)l + 2 \int_l^L f(z') \, dx + \rho g z^2(0)l + \rho g \int_l^L z^2 \, dx + 2E_s \qquad (1)$$

where prime denotes differentiation with respect to x, $f = f(z') = \alpha(z')(1 + z'^2)^{1/2}$, $\alpha(z')$ is the anisotropic surface energy per unit area of the crystal–liquid interface, g is acceleration due to gravity, $\rho = \rho_c - \rho_l$, ρ_c and ρ_l are the densities of the crystal and liquid, respectively; E_s is the interface-wall interaction energy [it depends on $z(L)$]. The free energy $\mathcal{F}$ must be minimal for a given crystal volume. By appropriately choosing the origin of the z axis, we can write the condition that the volume is constant in the form

$$l \cdot z(0) + \int_l^L z \, dx = 0 \qquad (2)$$

Using (1) and (2), and also the condition $z(1) = z(0)$ that the function $z(x)$ is continuous, one can easily verify that the condition $\delta\mathcal{F}/\delta l = 0$ that the free energy is minimal with respect to the flat part area is reduced to the continuity of $f(z(x))$ at $x = 1$. After simple transformations, the variation of free energy (1) can be represented as

$$\delta\mathcal{F} = \left\{ \eta(L) + \frac{\partial E_s}{\partial z(L)} \right\} \delta z(L)$$

$$- \int_l^L dx \, \delta z \left\{ \eta' - \frac{\eta_0}{l} - \rho g[z - z(0)] \right\} \qquad (3)$$

where $\eta(x) = \partial f/\partial z'$, $\eta_0 = \eta(1 + 0)$, the derivative of E_s with respect to $z(L)$ depends on the properties of the vessel walls and is equal to the difference $\alpha_s - \alpha_l$ between the surface energies of the crystal–wall and liquid–wall interfaces, respectively.

The condition that the free energy is minimal gives, by virtue of (3), the equation for calculating an equilibrium crystal shape

$$\eta' - \frac{\eta_0}{l} - \rho g[z - z(0)] = 0 \qquad (4)$$

and the boundary condition $\eta(L) = \eta_s$, where $\eta_s \equiv \alpha_l - \alpha_s$.

The thermodynamic properties of the interface are determined by the thermodynamic potential $f(z')$ satisfying the identity $df = \eta \, dz'$. Let us make the Legendre transformation by introducing the variable η instead of z' and a new thermodynamic potential $\tilde{f} = f - z'\eta$ satisfying the identity $d\tilde{f} = -z' \, d\eta$. It can easily be seen that the derivative $\eta' = -d\tilde{f}/dz$, so that the first integral of Eq. (4) is

$$\tilde{f}(\eta) - \tilde{f}(\eta_0) + \frac{\eta_0}{l}[z - z(0)] + \frac{1}{2}\rho g [z - z(0)]^2 = 0 \qquad (5)$$

If the potential $\tilde{f}(\eta)$ is known, the latter formula establishes a relationship η and z, and the surface shape is found by integrating the relation $dx = -d\eta/(d\tilde{f}/dz)$. In the case of $T < T_c$ of most interest is to calculate the area of the flat part. Precisely this quantity acts as a specific order parameter that characterizes the phase transition in question. Using (5), we obtain

$$L - l = \int_l^L dx = -\int_{\eta_0}^{\eta_s} \frac{d\eta}{(d\tilde{f}/dz)} = -\int_{|\eta_0|}^{|\eta_s|} \frac{d\eta}{\{\eta_0^2/l^2 - 2\rho g[\tilde{f}(\eta) - \tilde{f}(\eta_0)]\}^{1/2}} \qquad (6)$$

The particular form of the potential $\tilde{f}$ is different for faces of different symmetry,[10] but since the problem is one dimensional, in all the cases considered above we can use the same expression:

$$\tilde{f}(\eta) = f_0(t) - \frac{at}{2}\eta^2 - \frac{b}{4}\eta^4 \qquad (7)$$

Here $f_0(t)$ does not depend on η, a and b are positive constants, $t = T - T_c$. Since $z'(\eta) = -d\tilde{f}/d\eta$ and the parameter η_0 is defined by $z'(\eta_0) = 0$, we obtain

$$\eta_0^2 = \frac{a|t|}{b}, \qquad \tilde{f}(\eta) - \tilde{f}(\eta_0) = \frac{b}{4}\eta_0^4(\xi^2 - 1)^2$$

where $\xi = |\eta/\eta_0|$. Substitution into (6) yields

$$L - l = r_g \int_1^{|\eta_s/\eta_0|} \frac{d\xi}{[(\xi^2 - 1)^2 + (r_g/l)^2]^{1/2}} \qquad (8)$$

where $r_g \equiv r_g(t) = (2/\rho g a|t|)^{1/2}$.

As far as Eq. (8) is concerned, we should point out the following. Since in the derivation of this equation we used expansion (7) in the powers of η, this form of Eq. (8) is valid only when the limiting value η_s of η is small in

comparison with the characteristic surface energy α. The experimental values of the contact angle $z'(L) \sim 1$, so that $\eta_s \sim \alpha$. The fact is, however, that in the case of interest where the vessel size L is much larger than the capillary constant

$$r_g^{(0)} \sim r_g(t) \, |t/T_c|^{1/2} \sim (\alpha/\rho g)^{1/2} \sim 1 \text{ mm}$$

and the temperature T is close to T_c, the major contribution to integral (8) is due to the region of small η. Using relations derived above, it is a simple matter to verify that this contribution is caused by those values of ξ which are small as compared with α/η_0, so that the upper limit in (8) can be set equal to infinity. Thus, the final relation

$$L - l = r_g \int_1^{\infty} \frac{d\xi}{[(\xi^2 - 1)^2 + (r_g/l)^2]^{1/2}} \tag{9}$$

for determining l virtually does not depend on the wall properties. Far from the transition point, i.e., for $|t| \sim T_c$, the quantity r_g appearing in (9) coincides, by an order of magnitude, with the capillary constant $r_g^{(0)}$. As $t \to 0$, r_g grows infinitely as $|t|^{-1/2}$. In a sufficiently small neighborhood of the transition point the inequality $L \ll r_g$ holds, and we obtain from (9)

$$l = \frac{4}{\pi^3} \Gamma^4(3/4) \frac{L^2}{r_g} \tag{10}$$

where $\Gamma(x)$ is a gamma function. The size of the flat area is proportional to the vessel size squared and vanishes for $t \to 0$ as $|t|^{1/2}$, i.e., as the order parameter in the mean-field theory for ordinary second-order phase transitions.

If the temperature is not too close to the transition point, $L \gg r_g$ and from (9) we find to within the logarithmic accuracy

$$l = L - \frac{r_g}{2} \ln \frac{L}{r_g} \tag{11}$$

3. CRYSTAL SHAPE ABOVE THE TRANSITION POINT

For $T > T_c$ the interface does not have a flat part (Fig. 1b) and the equilibrium shape is determined from the condition that relation (1) (with $l = 0$) is minimal under the condition

$$\int_l^L z \, dx = \text{const}$$

The corresponding equation of equilibrium

$$\eta' - \rho g z + \lambda = 0$$

where λ is a Lagrangian multiplier, has the first integral

$$\tilde{f}(\eta) - \tilde{f}(0) + \tfrac{1}{2}\rho g z^2 = \lambda z \tag{12}$$

Integrating the relation $dx = -d\eta/(\partial \tilde{f}/\partial z)$ and using Eqs. (7) and (12), we obtain the implicit expression for the function $\eta(x)$

$$\frac{x}{r_g} = \int_0^\zeta \frac{d\zeta}{(\zeta^4 + 2\zeta^2 + A^2)^{1/2}} \tag{13}$$

where $\zeta = \eta(b/at)^{1/2}$ and $A = \lambda(2b/\rho g a^2 t^2)^{1/2}$ is a constant determined from the boundary condition $\eta(L) = \eta_s$. The equilibrium surface shape is defined by Eq. (13) and by the relation

$$z' = -\frac{\partial \tilde{f}}{\partial \eta} = \left(\frac{a^3 t^3}{b}\right)^{1/2} (\zeta + \zeta^3) \tag{14}$$

Let the temperature be so close to the critical temperature that $r_g \gg L$. Then from (13) and (14) we find for $x > 0$

$$|z'| = \left(\frac{2}{\rho g b}\right)^{1/2} \frac{\Gamma^4(1/4)}{16\pi L^2}\, atx \tag{15}$$

for $x \ll L^2/r_g$;

$$|z'| = \left(\frac{2}{\rho g}\right)^{3/2} b^{-1/2} \left[\frac{\Gamma^4(1/4)}{16\pi L^2}\right]^3 x^3 \tag{16}$$

for $L^2/r_g \ll x \ll L$;

$$|z'| = \left(\frac{2}{\rho g}\right)^{3/2} b^{-1/2} (L - x)^{-3} \tag{17}$$

for $r_g^{(0)} \ll |L - x| \ll L$ [the corresponding relations for $x < 0$ are obtained by using the condition $z(x) = z(-x)$].

In the immediate proximity to the wall, for $|L - x| \lesssim r_g^{(0)}$, the surface shape depends both on the behavior of the potential $\tilde{f}$ for not very small η and on the particular value of the parameter η_s, so that this shape cannot be calculated in a general case.

For temperatures not too close to T_c, such that $r_g \ll L$, we obtain

$$|z'| = \left(\frac{32\rho g}{b}\right)^{1/2} a^2 t^2 x \exp\left(-\sqrt{2}\,\frac{L}{r_g}\right) \tag{18}$$

for $x \ll r_g$, and Eq. (14), in which

$$\zeta = \frac{\sqrt{2}}{\sinh[\sqrt{2}\,(L-x)/r_g]} \tag{19}$$

for $x \gg r_g$.

It should be noted that if the transition point is approached from the region of higher temperatures, the interface curvature $z''(0)$ at the center of the vessel first increases exponentially, in accordance with Eq. (18), and only for $t \ll T_c(r_g^{(0)}/L)^2$ drops proportionally to t, in accordance with Eq. (15).

By dedicating this paper to the memory of late Ilya Mikhailovich Lifshitz, we highlight a profound impact he exerted on the advancement in this field of physics.

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