

# Equilibrium shape and oscillations of the surface of quantum crystals

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Allowance for the quantum effects is used to explain the experimentally observed absence of faceting of helium crystals. It is shown that weakly damped melting and crystallization waves may be propagated along an  $\text{He}^4$ -liquid interface. The temperature dependence of the surface tension is found at low temperatures.

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According to the classical ideas (see, for example, Ref. 1-2) a macroscopically homogeneous surface of a crystal which is in equilibrium with a liquid or vapour can be atomically smooth or atomically rough. In the former case the crystal has a characteristic faceting with flat parts of the surface and in the other it has a spherical shape. The quantitative criterion is the absolute value of the transition entropy  $\Delta S$ , i.e., of the difference between the entropies of the two phases in contact calculated per particle. The  $\Delta S \geq 1$  case corresponds to an atomically smooth surface and  $\Delta S \leq 1$  to a rough one. In the case of conventional classical crystals the transition entropy increases without limit on reduction in temperature and, therefore, at a sufficiently low temperature a crystal should have an atomically smooth surface.

A characteristic situation appears in crystals of helium isotopes which may be in equilibrium with a liquid at any temperature no matter how low. Since at absolute zero the entropies of both phases vanish, the transition entropy is small. Formal application of the classical criterion predicts<sup>3</sup> an atomically rough helium surface. Although the available experimental results<sup>3,4</sup> (absence of faceting and of significant supercooling even at high growth rates) do confirm this conclusion, the use of the classical criterion is not permissible. A surface which is atomically rough in the classical sense cannot be in equilibrium at absolute zero because its entropy is not equal to zero. The experimentally observed effects, like the very existence of a crystal-liquid interface at absolute zero, can be explained only by a suitable allowance for the quantum effects. We shall show that the phase boundary between a quantum crystal and a quantum liquid may be in a special state which is a quantum analog of an atomically rough surface.

1. Delocalization of particles in a quantum crystal means that the microscopic structure of such a phase boundary cannot be represented in the same literal way as is done for classical crystals. However, such concepts as a surface step and a kink in the step (Fig. 1) can also be introduced in the quantum case. It is sufficient to use the general properties of a boundary which follow from the symmetry of phases in contact.

For example, the surface step corresponds to such a state of the boundary in which its positions at infinity (to the right and left in Fig. 1) are shifted by an elementary translation vector of the crystal and the energy of the system has the lowest possible value. In view of the periodicity of the crystal and homogeneity of the liquid, a shift by one translation vector transforms the boundary to an equivalent position and, therefore, a step is a linear defect on the surface and only this property of the step is important in our analysis.

Let us assume that  $\beta$  is the energy of a step per unit length equal to an elementary translation vector. According to Landau,<sup>5</sup> if  $\beta$  is finite then the derivative  $\partial\alpha/\partial\varphi$  of the surface tension with respect to the angle  $\varphi$  between the normal to the boundary and the [001] direction exhibits a finite jump proportional to  $\beta$  when  $\varphi = 0$ . This discontinuity of the function  $\partial\alpha/\partial\varphi$  necessarily gives rise to flat parts in the equilibrium shape of a crystal and these parts increase in size with the jump of the derivative  $\partial\alpha/\partial\varphi$ . Thus, the faceting of a crystal is connected directly to the finite value of  $\beta$ . In the case of classical crystals at absolute zero the value of  $\beta$  is always finite and, therefore, at low temperatures such crystals are always faceted. This is also possible in the case of quantum crystals. However, it is interesting to note that in the case of a quantum crystal the energy of a step may be exactly zero.

The state of a step is governed by the configuration of the kinks in it and the kinks have two opposite "signs" (Fig. 1). Each kink can be regarded as a point defect on a step. The kink energy does not change when it is displaced by a translation vector because such a

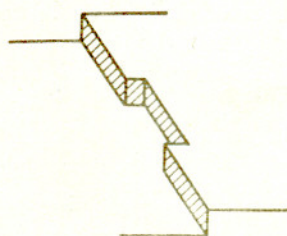


FIG. 1.

displacement involves the transfer of matter from one phase to another without a contribution to the energy since the chemical potentials of the phases in equilibrium are equal. Therefore, like other point defects,<sup>6</sup> a kink on the surface of a quantum crystal behaves as a delocalized quasiparticle whose state is governed by the quasimomentum. Here, we encounter the following circumstance which is important in the subsequent treatment. Let  $p_0$  be the value of the quasimomentum corresponding to the bottom of an energy band. At absolute zero this state is stationary (and ground) for an isolated kink and the velocity of the kink is zero. Stationary states of similar energies ( $p \rightarrow p_0$ ) correspond to a finite kink velocity. Thus, an isolated kink is an example of a system which has states whose energies can be as close as we please to the ground state and which are characterized by a continuous flux of matter from one phase to the other.

If the width of the energy band of kinks  $\Delta$  is sufficiently great ( $\Delta/2 > \epsilon_0$ , where  $\epsilon_0$  is the energy of a localized kink), the energy near the band bottom becomes negative. Then, the total energy of a step decreases on appearance of kinks with  $p = p_0$  and the structure of the ground state of a step can be found only if allowance is made for the interaction between kinks.

Collision of two kinks of any sign results in exchange of their quasimomenta (Fig. 2a). In the case of kinks of one sign this is the only possible elastic process; however, if the signs of the kinks are opposite, there is also a possibility of a "jump" to the next row, in which each kink retains its quasimomentum (Fig. 2b). Moreover, bearing in mind that over long distances the interaction is of the van der Waals type, we can easily see that the kinks interact over long distances in accordance with the law  $U(r) \propto \epsilon_0(a/r)^4$ , where  $a$  is the interatomic distance, and that kinks of opposite sign become attracted, whereas those of the same sign repel. It is therefore clear that the interaction between kinks is important only over atomic distances.

An increase in the concentration of kinks in a step thus reduces the energy of the latter until the concentration becomes of the atomic order. The minimum energy is then

$$\beta \approx \beta_0 + \epsilon_0 - \Delta/2,$$

where  $\beta_0$  is the energy of a rectilinear "bare" step without kinks.

In the case of classical crystals the quantities  $\beta_0$  and  $\epsilon_0$  are of the order of the difference between the

energies of two phases in contact taken per one atomic bond.<sup>1</sup> In the case of helium, such an estimate gives  $\beta_0 \approx \epsilon_0 \approx 0.1$  °K. However, the value of  $\Delta$  is expected to be of the order of 1 °K. Therefore, it seems very likely that the energy of the ground state of an isolated step is negative. Moreover, it follows from the above discussion of the motion of an isolated kink and of the nature of the possible interactions of kinks with one another that there are states of a step which are close in energy to the ground state and that these states correspond to continuous motion of a step, accompanied by the transfer of particles between the phases.

If the energy of an isolated step is negative, then an atomically smooth surface of a crystal is unstable in respect of step creation. As a result, an equilibrium surface should become a type of two-dimensional liquid consisting of delocalized steps of various configurations, including closed steps of finite length. It is important to note that the number of steps of each kind in such liquid is not fixed and is governed by the condition of minimal energy. Therefore, the energy of a step  $\beta$ , which is the derivative of the total energy with respect to the number of steps, vanishes in equilibrium.

This vanishing of the step energy means that the surface tension  $\alpha$  is a smooth function of the orientation of the normal for directions described by small Miller indices (as mentioned above, the discontinuity of the derivative  $\partial\alpha/\partial\varphi$  is proportional to the step energy  $\beta$ ). For (011) type faces, where  $l$  is a large number, the discontinuity in  $\partial\alpha/\partial\varphi$  is due to<sup>5</sup> the appearance of superstructures in the positions of steps on faces of the (0,  $L$ ,  $Ll+1$ ) type which can be as close as we please to a (011) face. This mechanism is clearly possible only in the case of localized steps. In the case under discussion the quantum-mechanical delocalization makes superstructure steps impossible and the derivative  $\partial\alpha/\partial\varphi$  is continuous also for these faces. Thus, crystals with a surface of the type considered here are always characterized by a smooth  $\alpha(\varphi)$  function and, therefore, they do not become faceted.<sup>1)</sup>

The growth of a crystal with such a surface takes place both by an increase in the surface bounded by each step and by formation of new atomic layers on collision of two steps (this process is analogous to a jump into the next row on collision of two kinks). It is important to note that these and reverse processes give rise to stationary states of the system, which can be as close as we please to the ground state and that continuous growth or melting of a crystal occurs via these states. The motion of a phase boundary at absolute zero thus occurs without disturbing the phase equilibrium. In other words, the kinetic growth coefficient  $K$ —defined by the formula  $V = K\Delta\mu$ , where  $V$  is the velocity of the boundary and  $\Delta\mu$  is the difference between the chemical potentials of the phases in contact—becomes infinite at absolute zero for a crystal with this type of surface.

At finite temperatures the motion of a phase boundary is accompanied by dissipation due to the interac-

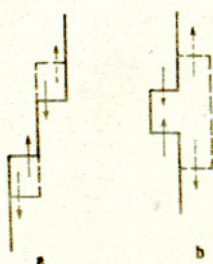


FIG. 2.

tion with thermal phonons. The energy dissipated per unit time and per unit surface area is of the order of  $E_{ph}(V/c)V$ , where  $c$  is the velocity of sound,  $E_{ph} \propto nT^4/\Theta^3$  is the phonon energy,  $n$  is the number of atoms per unit volume, and  $\Theta$  is the Debye temperature. On the other hand, the same dissipated energy is equal to  $\Delta\mu N$ , where  $N \sim nV$  is the number of atoms transferred per unit time from one face to the other. Hence, we find that

$$K \propto c\Theta^3/T^4. \quad (1)$$

We can thus see that the growth coefficient becomes infinite in the limit  $T \rightarrow 0$  which it approaches proportionally to  $T^{-4}$ .

It should be noted that the ranges of validity of Eq. (1) are very different for crystals of the helium isotopes  $\text{He}^3$  and  $\text{He}^4$ .

In the case of  $\text{He}^4$  the validity of Eq. (1) requires simply that phonons be the main type of thermal excitation in the liquid phase. As is known, this condition is satisfied at temperatures below approximately 0.6°K. At high temperatures, instead of the power law, we now have the exponential dependence  $K \propto \exp \times (\Delta_r/T)$ , where  $\Delta_r$  is the roton gap.

In the case of  $\text{He}^3$  crystals, Eq. (1) can be applied only at extremely low temperatures, much lower than the temperature of transition to the superfluid state. At higher temperatures, when liquid  $\text{He}^3$  behaves as a Fermi liquid, the main dissipation mechanism is the interaction of a moving boundary with Fermi excitations. The energy dissipation is of the order of  $p_F nV \cdot V$ , where  $p_F$  is the momentum on the Fermi surface, which corresponds to a temperature-independent growth coefficient  $K \propto 1/p_F$ .

2. We shall show that weakly damped oscillations, similar to capillary waves at a liquid-vapor interface, may propagate along an interface between a quantum crystal and liquid. However, they are different because capillary waves correspond to the motion of matter near the surface in the absence of evaporation and condensation processes. Our waves are entirely due to periodic melting and crystallization.

Let us assume that a flat surface  $z = 0$  undergoes a displacement  $\xi(x, t) = \xi_0 e^{ikx - i\omega t}$  in the direction of its normal. The motion which appears in a liquid is described by the potential  $v = \nabla\psi$ , where  $\psi = \psi_0 e^{ikx - k_1 z - i\omega t}$ . The liquid can be regarded as incompressible because, as we shall see later, the phase velocity of the oscillations under discussion is much less than the velocity of sound. The boundary conditions at  $z = 0$  are

$$v_z = \frac{\rho_2 - \rho_1}{\rho_2} \dot{\xi}, \quad \mu_1 - \mu_2 = 0, \quad P_2 - P_1 = \left( \alpha + \frac{\partial^2 \alpha}{\partial \varphi^2} \right) \frac{\partial^2 \xi}{\partial x^2}. \quad (2)$$

Here,  $P$  is the variable part of the pressure;  $\rho$  is the density;  $\varphi$  is the angle between the normal to the displaced surface and the  $z$  axis; the indices 1 and 2 refer to the solid and liquid phases, respectively.

Since

$$P_2 = -\rho_2 \psi, \quad \mu_1 - \mu_2 = m \left( \frac{P_1}{\rho_1} - \frac{P_2}{\rho_2} \right),$$

where  $m$  is the mass of an atom, we find that the oscillation spectrum is

$$\omega^2 = \left( \alpha + \frac{\partial^2 \alpha}{\partial \varphi^2} \right) \frac{\rho_2}{(\rho_1 - \rho_2)^2} k^3. \quad (3)$$

If the gravity  $g$  is allowed for, an additional term  $\rho_2 g k / (\rho_1 - \rho_2)$  appears on the right-hand side of Eq. (3).

Like the conventional capillary waves, the oscillations described by Eq. (3) are unstable in respect of dissociation of one quantum into two of lower energy. Therefore, the oscillations in question are characterized by finite damping even at  $T = 0$ . The order of magnitude of the damping coefficient  $\gamma$  (reciprocal of the lifetime) is given by  $\gamma \sim \hbar k^5 / \rho$  (see Ref. 7, where the problem is solved for the conventional capillary waves).

At finite temperatures and for low-frequency oscillations the second damping mechanism associated with the finite growth coefficient  $K$  is the more important. We can calculate the corresponding damping coefficient by including the quantity  $-\dot{\xi}/K$  on the right-hand side of the second condition in Eq. (2). If we assume that the damping is weak, we find that

$$\gamma = \frac{\rho_1 \rho_2 k}{2mK(\rho_1 - \rho_2)^2}. \quad (4)$$

In the case of  $\text{He}^3$ , within the range of validity of the theory of Fermi liquids, the application of the above estimate of  $K$  leads to the conclusion that the oscillations in question are strongly damped at all frequencies. In the case of  $\text{He}^4$  at low temperatures, the substitution of Eq. (1) into Eq. (4) shows that there is a wide range of wave vectors  $ka \gg (T/\Theta)^{1/3}$  in which the wave damping is weak. Experimental observation of these waves will give a direct proof that  $\text{He}^4$  crystals have a boundary of the type discussed above.

3. Oscillations with the spectrum (3) are elementary excitations of the  $\text{He}^4$  crystal-liquid interface at low temperatures. They are responsible for the temperature dependence of the surface tension. Since according to Eq. (3) the frequency is, as in the case of capillary waves at a liquid-vapor interface, proportional to  $k^{3/2}$ , the temperature dependence of the surface tension is the same for crystal-liquid and liquid-vapor interfaces. The temperature-dependent component of the surface tension is proportional to  $T^{7/3}$  (see Ref. 8).

A similar situation occurs also in the case of  $\text{He}^3$  in the range of applicability of the theory of Fermi liquids to the liquid form of this isotope. The temperature dependence of the surface tension at crystal-liquid and liquid-vapor interfaces is then mainly due to the contribution of Fermi excitations. The temperature-dependent component of the surface tension is now

proportional to  $T^2$ , which is clear from the following simple considerations. The free energy of a Fermi system always varies proportionally to the square of temperature and level density near the Fermi surface. The presence of the surface affects only the density of levels which can be represented as the sum of the volume and surface components. The surface tension coefficient, which is the surface part of the free energy, varies proportionally to the surface component of the level density and to the square of temperature.

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<sup>1)</sup>Strictly speaking, such a surface can have ridges separating circular parts and corners. A crystal can have a completely spherical shape if the condition  $\alpha + \partial^2\alpha/\partial\phi^2 > 0$  is obeyed along all directions.<sup>1</sup>

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