Nature of faceting phase transitions of crystals

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A mechanism which would make any crystal surface atomically rough at any nonzero temperature is pointed out. The nature of the phase transitions observed experimentally, in which crystals become faceted, and the relationship with the dissipationless crystallization of quantum helium crystals are discussed.

Research on the interfaces of crystalline and superfluid liquid ^{4}He (Refs. 1–4) and several other systems[5] has revealed surface phase transitions which are manifested experimentally as the appearance of a faceting of the crystal as the temperature is lowered. In the theory (see the reviews[6,7]) these phase transitions are customarily linked with transitions of the crystal surface from an atomically rough state to an atomically smooth state. The results found through studies of several exactly solvable models and through a renormalization-group analysis have shown[6,7] that such transitions must be (Berezinskiĭ–) Kosterlitz–Thouless transitions.

Experimental results on the nature of the phase transitions at the surface of ^{4}He crystals both support[8] and speak against[9,10] the Kosterlitz–Thouless picture. Recent direct measurements of the anisotropy of the thermodynamic properties and the kinetics of the surface of ^{4}He crystals[11,12] clearly contradict that picture.

In this letter we would like to call attention to a mechanism, not considered in previous theories, which would rule out an atomically smooth state of a crystal surface at any (nonzero) temperature. In this manner it is shown that there can be no equilibrium faceting of crystals (at a nonzero temperature) and that there can be no roughening phase transitions ("roughening transition" is the English-language term), to which the Kosterlitz–Thouless picture actually applies. The phase transitions observed experimentally are actually accompanied by the appearance of a kinetic faceting. Depending on whether the temperature is or is not above the phase-transition temperature, the crystal which arise in the growth process will be respectively unfaceted or faceted. It is in this sense that we will be discussing "faceting" phase transitions of crystals.

1. Fluctuations play a key role in the question of the state of a surface.[7,13] We denote by $z = z(\mathbf{r})$ the equation of the crystal surface, taking fluctuations into account, and we denote by $\mathbf{r} = (x,y)$ a two-dimensional coordinate. The equilibrium state corresponds to $z = \langle z(\mathbf{r}) \rangle = 0$. In general, a displacement $z(\mathbf{r})$ of surface points from their equilibrium position is a sum $z(\mathbf{r}) = \zeta(\mathbf{r}) + u(\mathbf{r})$ of a "growth" displacement $\zeta(\mathbf{r})$ and an "elastic" displacement. The displacement ζ corresponds to a growth or melting of the crystal, while the displacement u is the z component of the displacement vector in the theory of elasticity. It corresponds to a displacement of the surface along with the crystal lattice. The growth displacement ζ is, in general, a displacement

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$z - u$ of surface points with respect to the crystal lattice. Let us consider the correlation function

$$G(\vec{r}) = < [\zeta(\vec{r}) - \zeta(0)]^2 > . \quad (1)$$

A surface of any rational initial orientation is atomically smooth or atomically rough, depending on whether $G(\infty)$ is finite or infinite.[7,13] To demonstrate the point, we assume that $G(\infty)$ has a finite value. In this case the effective thickness of the surface in the coordinate system of the lattice is finite. When such a surface is displaced (by the growth method) one lattice period in the perpendicular direction from its original position, it goes into a state which is crystallographically equivalent to the original state but nevertheless different. The latter statement means (see the corresponding discussion in Ref. 7) that the energy of growth steps on this surface is positive, i.e., that the surface is atomically smooth. A rational surface is atomically rough, i.e., characterized by a zero step energy, if its "growth" thickness is infinite,i.e., if $G(\infty) = \infty$. In this sense, a surface of irrational orientation will always be atomically rough.

In a theory of the Kosterlitz–Thouless type the assumption $u \equiv 0$ is made. If dislocation degrees of freedom of the crystal are ignored, this assumption is in fact legitimate, since the fluctuations of the displacement vector due to the phonon degrees of freedom are finite for a three-dimensional crystal. When we take dislocations into account, we find a different situation.

Let us consider the fluctuations of a surface associated with the presence of thermal fluctuational defects of the type shown in Fig. 1. This defect is similar to the

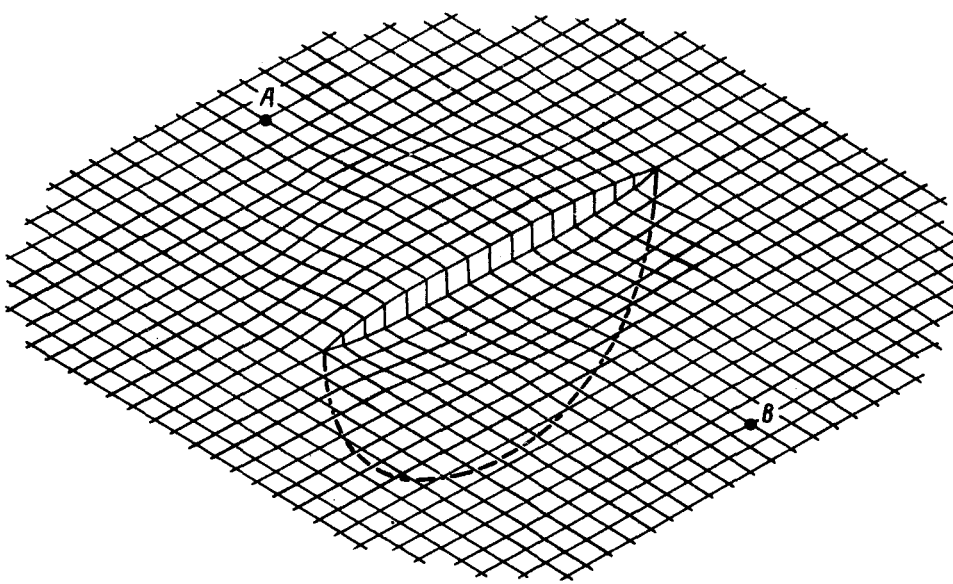

FIG. 1. The defect of interest on a crystal surface. This defect consists of a growth step of finite length and a dislocation in the form of a semicircle.

Frank–Read source in the theory of crystal growth.[7] It consists of a step of finite length on the crystal surface and of a dislocation in the adjacent volume, in the form of a semicircle that connects the ends of the step. The Burgers vector of the dislocation runs perpendicular to the surface, so the dislocation is a screw dislocation near its ends but an edge dislocation near its center. It is important to note that the change in the growth displacement along line AB (Fig. 1; points A and B are far from the defect) is

$$\Delta\zeta = \int_A^B d\zeta = -a,$$

where a is the lattice constant. The corresponding change in the elastic displacement is $\Delta u = +a$, so the change in the total displacement, Δz, is zero.

We denote by 0 and $\mathbf{r}$ two points on the surface which are separated by a macroscopic distance r. We consider the points at which the line connecting 0 and $\mathbf{r}$ intersects defects of the type described above. The difference between the growth displacements, $\zeta(\mathbf{r}) - \zeta(0)$, is $a(N_+ - N_-)$, where N_+ and N_- are the number of points of "positive" and "negative" intersections. Since each defect is characterized by a finite step length l and a finite energy ϵ, the average numbers of intersections are, in order of magnitude,

$$< N_+ > = < N_- > = N \sim (r/l)e^{-\epsilon/T}.$$

The correlation function is determined by

$$G(\vec{r}) = < [\zeta(\vec{r}) - \zeta(0)]^2 > \sim a^2 < (\delta N)^2 > \sim a^2 N \sim r(a/l)^2 e^{-\epsilon/T}. \qquad (2)$$

At large values of r, this function increases in proportion to r,i.e., much more rapidly than the $\ln r$ increase predicted by a theory of the Kosterlitz–Thouless type. This behavior of the correlation function as a result of ordinary fluctuations in crystallization or melting occurs for a one-dimensional boundary.[7] For such a boundary, and for the same reason as in our case, fluctuations destroy the atomically smooth state. At any nonzero temperature the surface of a three-dimensional crystal is thus atomically rough.

2. This result shows that the three phase transitions which are observed on the surfaces of ^{4}He crystals at temperatures of 1.2, 0.9, and 0.35 K are not transitions between atomically smooth and atomically rough states. The surfaces of all three orientations are atomically rough, both above and below these transitions. A thermodynamically equilibrium faceting should not arise at any nonzero temperature. This fact agrees with the experimental results of Refs. 9–12, where all attempts to measure the equilibrium size of the faceted parts of a surface (or the equivalent magnitude of the jump in the angular derivative of the surface energy) met with failure. All that was found possible to do was to establish an upper limit on this size, which turned out to be extremely small. On the other hand, it has been established experimentally[11,12] that all three of these transitions are of the same nature, so the following picture of these transitions seems quite natural.

From the thermodynamic standpoint, a singular orientation of the surface of a

crystal arises below the point of the transition. Near this orientation ($\theta \to 0$) the angular dependence $\gamma(\theta)$ of the surface stiffness[11,12] has either a power-law singularity

$$\gamma(\theta) = A\theta^{-\alpha} \tag{3}$$

with a small power $\alpha \approx 0.2$ or a logarithmic singularity

$$\gamma(\theta) = B\ln(\theta_0/\theta), \tag{4}$$

where A, B, and θ_0 are positive constants. Above the transitions, the singularity in $\gamma(\theta)$ disappears. At the point of the transition, the nature of the dependence of the crystal growth rate v on the difference between the chemical potentials on the two sides of its surface, $\Delta\mu$, changes. This dependence has been measured by Wolf *et al.*[8] Above the transition, with small values of $\Delta\mu$, we have $v = K\Delta\mu$, where K is a growth coefficient. At all temperatures below the point of the transition on the singular face itself ($\theta = 0$) we have $K = 0$, and at small values of $\Delta\mu$ we have

$$v = L(\Delta\mu)^{\delta}, \tag{5}$$

where L is a constant, and $\delta > 1$. The power-law nature of expression (5) seems natural since the energy of the steps on a singular surface is zero, but it is the nonzero energy of a step that is responsible for the exponential dependence $v(\Delta\mu)$ for atomically smooth surfaces.

The angular dependence of the growth coefficient near the singular orientation ($\theta \to 0$) is described at temperatures below the critical temperature by

$$K(\theta) = K_0\theta^{\beta}, \tag{6}$$

where K_0 is a constant (a function of the temperature), and where, according to Refs. 11 and 12, we have $\beta \approx 1$.

Figure 2 is a full logarithmic plot of the experimental data of Wolf *et al.*[8] on the growth rate of ^{4}He crystals with a (0001) surface below the transition temperature. The solid straight lines correspond to Eq. (6) with a temperature-independent parameter $\delta = 5/3$. At very small values of $\Delta\mu$, the dependence $v(\Delta\mu)$ in Fig. 2 is exponential. This behavior of the growth rate can be attributed to a pinning of the interface at lattice defects, which would unavoidably occur at sufficiently small values of $\Delta\mu$.

We know that an anisotropy of the growth coefficient as in (6) gives rise to a kinetic faceting of crystals as they are grown. An assertion we are making on the basis of our experimental study is that this sort of nonequilibrium faceting has been observed in all experiments. The relaxation times of the kinetic faceting may be extremely long because of the pinning processes that we just mentioned, Keshishev *et al.*[9] have pointed out a similar possibility for explaining the lack of success in measurements of the size of the equilibrium faceting.

3. At absolute zero, all rational surfaces are atomically smooth[13] (the energy of a step is positive), while irrational surfaces are atomically rough. One might say that irrational surfaces of quantum ^{4}He crystals are in a quantum-mechanically rough state at $T = 0$, a state characterized by a dissipation-free crystallization (an infinite growth coefficient[14]). At a nonzero temperature there is no faceting, so the fraction of the

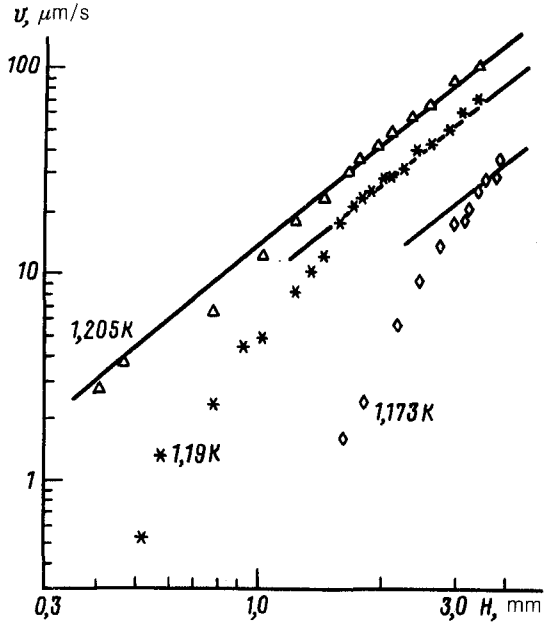

FIG. 2. Experimental data on the growth rate of ^{4}He crystals with a (0001) surface at temperatures $T = 1.205$, 1.19, and 1.173 K below the transition temperature.[8] v—Growth rate; $H = [\rho_s/(\rho_s - \rho(t))g]\Delta\mu$—difference between levels; $\rho_{(l)}, \rho_s$—densities of liquid and solid helium.

total area of the equilibrium surface occupied by rational orientations is zero, and the picture of a "quantum-mechanical roughness" applies to essentially the entire surface. The result found in § 1 of this letter thus shows that the experimental conclusion that crystallization waves and other phenomena exist (see the review article by Lipson and Polturak[15]), and that they are related to a quantum-mechanical roughness of a surface and a dissipation-free crystallization, is in total agreement, from the theoretical standpoint, with the assertion that any rational surface is atomically smooth at absolute zero.

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