

EQUILIBRIUM CRYSTAL SHAPES

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Abstract

This paper presents a basic understanding of Equilibrium Crystal Shapes from a thermodynamic and statistical point of view. Willif's plot is drawn for a naive 2d system of only nearest-neighbor interactions. Using this insight it is possible to construct a phase diagram for a similar 3d model. The solid-on-solid model is reviewed to describe critical behavior within the Kosterlitz-Thouless universality class for a 2d interface. Quantum roughening is addressed briefly. Two experiments are described: report of a third roughening temperature for the He interface which reinforces the absence of quantum roughening for this system, and a calculation of the Pokrovsky-Talapov exponent of lead crystals.

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1 Introduction

Generally, crystals are of polyhedral shape, the shapes of the faces and the angles of contact between them determined by symmetry, crystal anisotropy and conditions of growth. The equilibrium form, i.e. the equilibrium crystal shape, is not the shape observed under ordinary conditions. The equilibrium shape is determined by the condition of the free energy F , or more exactly, [Landau] the thermodynamic potential for the given crystal volume, to be a minimum.

Most crystals grow under conditions that are far from equilibrium. The familiar forms which result are determined by growth kinetics rather than equilibrium considerations. In fact, re-equilibration requires transport of material over long distances, and time scales can be realistically long [Rottman]. For certain special systems equilibrium can, nevertheless, be achieved. For example, the equilibrium shape of ^4He crystals is completely rounded above about 1.17 K, no flat regions exists. Below this temperature there are planar regions in the crystal shape called "facets". Other systems behave alike: (i) plastic crystals of C_2Cl_6 or NH_4Cl show well defined facets only below 100 °C. (ii) equilibrium shapes of small lead and gold exhibit both round parts and facets (similar to ^4He crystals) at temperatures around 200 °C (Pb) and 1000 °C (Au), respectively, (iii) anomalies in the Debye-Waller factor of high index surfaces of copper around 200 °C have been interpreted as being due to faceting. The appearance or vanishing of a given facet at a fixed temperature is associated with the so-called "roughening transition" of that facet.

The present paper plan to give a glimpse in this rather extensive and old field which might turn out to be essential in nanotechnology. I will show in section 2 the problem of faceting of a crystal shape using mainly thermodynamic arguments. Section 3 explains the roughening transition using the solid-on-solid model and it is discussed the phase diagram and the problem of quantum roughening. Section 4 deals with some experimental results on ^4He crystals and Pb-crystals.

All the considerations apply to thermal equilibrium, non-equilibrium phenomena like dendritic growth shapes are not considered.

2 Faceting

2.1 Surface free energy

Macroscopic equilibrium crystals can only exist under conditions of temperature T and chemical potential μ which are consistent with bulk coexistence of a solid phase with a fluid phase, i.e., and this is the key point, one or both of the coexisting phases must be anisotropic. The thermodynamic properties of such an interface are entirely described by one quantity, the surface free energy F or equivalently, the surface free energy per unit surface area γ . [1], [14].

$$F_{s-w,f}(T, \omega) = \oint_{\partial\omega} \gamma(\hat{n}, T) dS \quad (1)$$

where we have set the following conditions: N is the fixed number of particles, given T , and μ , in a large fixed volume Ω so as to create a macroscopic inclusion ω of solid phase in the surrounding fluid. $V(\omega)$ is the volume of ω ; $S(\omega)$ is the area of the surface $\partial\omega$ of ω ; and similarly for Ω . Given $\gamma > 0$ the interface tends to become as small as possible (for a given volume of the two phases). Besides $\gamma(\hat{n})$, just called the surface energy, depends on the face orientation for an anisotropic body, i.e. for a crystal.[14]

The thermodynamics of crystal shapes is based on the proposition that a macroscopic inclusion of fixed volume

$$V(\omega) = \int_{\omega} dV \quad (2)$$

(i.e. fixed N) takes at equilibrium that shape which minimizes the surface free energy (1) subject to the constraint (2). Nontrivial shapes are the consequence of the \hat{n} dependence of γ , which in turn results from the breaking of spherical symmetry in the formation of the solid. When two isotropic phases coexist, the \hat{n} dependence is absent and inclusions are spherical. (e.g. raindrops)+ [1]

This minimization problem was originally solved by Wulff [1]. The recipe can be described as follows:

- (a) Make a polar plot (the Wulff plot) of the surface energy $\gamma(\hat{n}, T)$ as a function of \hat{n} .
- (b) Starting at the origin, draw the radius in direction \hat{n} out to the Wulff plot.
- (c) Construct a plane perpendicular to \hat{n} through the intersection of the radius with the Wulff plot.
- (d) Repeat for all directions \hat{n} .

The envelope of this family of planes $\tau(\hat{h}, T)$ is the equilibrium crystal shape. \hat{h} is the appropriate angular variable describing the crystal shape (see Fig. 1). Note that $\tau(\hat{h}, T)$ is the Legendre transform of $\gamma(\hat{n}, T)$, where \hat{h} and \hat{n} are the conjugate variable, because the plane perpendicular to \hat{n} is tangent to ECS at a point (or points) labeled \hat{h} (this could be a geometrical definition of the Legendre transformation). This τ is a free energy and its singularities define an interfacial face diagram. This is appealing idea: the fact that the crystal shape itself may be regarded as a free energy. In which other system does nature provide her own model of the free energy surface?

Furthermore, the convexity of the physical crystal shape is just the analog of the convexity of the magnetic free energy $f(H, T)$. Thus the classification

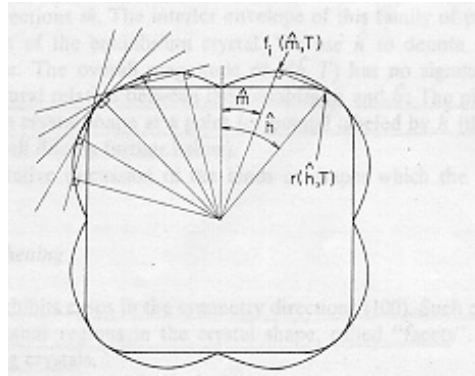


Figure 1: Wulff Plot

of phase transition according whether $\partial f / \partial H$ is (first order) or is not (second order) nonanalytical is stated in ECS by looking over whether singular points of the crystal shape do or do not correspond to sharp or smooth edges.[1]

2.2 Cusps, facets and roughening

The phenomenon of equilibrium faceting plays the key role in determining the equilibrium crystal shape [4]. Facets are plane sections each of which corresponds to the emergence to the surface of a crystal face with definite Miller indices [15]. Let be a nearest-neighbor lattice model at $T=0$. To form an interface between A and B, a total of $(|X| + |Y|)$ bonds must be cut. Let be energy per bond ϵ , then the minimum total energy required is $\epsilon(|X| + |Y|)$ and the energy per unit length is [1]

$$\gamma(\hat{n}, T = 0) = \frac{\epsilon(|X| + |Y|)}{\sqrt{X^2 + Y^2}} = \epsilon(|\cos \theta| + |\sin \theta|) \quad (3)$$

Here it is why the surface energy is cusped in the symmetry directions, this for small θ

$$\gamma(\hat{n}, T = 0) = \epsilon(1 + |\theta|) \quad (4)$$

To reach B from A we have to make several steps (Fig. b) which increase up to a maximum for $\theta = 45^\circ$ as it is expected from Wulff's plot. For $T > 0$ (Fig. c) thermal fluctuations modify the $T=0$ step energies, and the coefficient of $|\theta|$ becomes the free energy per unit step length. It is been shown [Weeks] that the step free energy decreases with increasing temperature and vanishes in a singular manner at a "roughening temperature" T_R , which for simple $d = 3$ (bulk) lattice models is typically about half of the bulk critical temperature

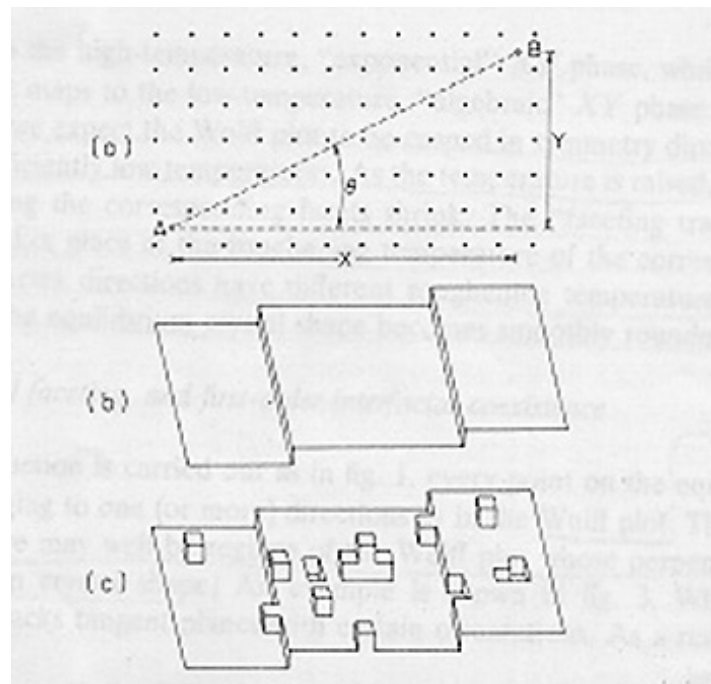


Figure 2: Steps and ledges on crystal surfaces. (a) An interface joining A and B must cut at least $|X| + |Y|$ nearest-neighbor bonds. (b) A system of steps or ledges on an $(hk0)$ interface at $T = 0$. (c) Thermal excitations modify the ledge system at $T > 0$; however a (renormalized) step free energy per unit length remains well-defined and nonzero for all $T < T_K$.

T_c . The singularity of this roughening temperature is in the same universality class as the Kosterlitz-Thouless transition [Rottman] of the $d=2XY$ model (see below).

This as a summary we have found that the orientational dependence of the surface free energy $\gamma(\hat{n}, T)$ is expected to have cusps in symmetry directions leading to facets in the crystal shape at sufficiently low temperatures. These cusps represent discontinuities being associated with the free energy of the steps on a given facet, i.e. this function has discontinuous derivatives everywhere [15]. As the temperature is increased, steps free energies decrease, cusps blunt, and the corresponding facets shrink. A given facet will finally disappear at the roughening transition temperature T_R of the corresponding infinite planar surface, T_R being different for different symmetry directions, i.e. T_R is an anisotropic quantity. Above T_R the corresponding region of the equilibrium crystal shape becomes smoothly rounded. The concept of faceting phase transitions was introduced by Burton and Cabrera.[3],[4]

Besides the planar parts, the crystal surface may contain singular lines and points at low temperatures. The first of them are the so called edges, along which finite jumps occurs in the orientation of the normal to the surface; the second are conical (or angular) points, near which the crystal surface has the shape of a cone. The appearance of these anomalies as the temperature is lowered also determines a set of critical temperatures characteristic of the given crystal.

In addition at $T = 0$ it is generally believed that ECS are entirely faceted, although there has been some controversy due to quantum roughening (see below). Interactions will distort the naive Wulff picture described. Depending on their magnitude and size can stabilize a finite number of facets or lead to an infinite number or dense facets over \hat{h} (Devil's staircase) [1][12]

Finally, it is important to stress the fact that steps and kinks which occur on the surface of the crystal are interacting statistical objects. Then the ECS results from an equilibrium distribution on these. In fact, the nucleation or annihilation of steps and motion of existing steps can be used to interpret the growth and melting of crystals. [5]

3 The roughening transition

There are several models which describes roughening transitions. To illustrate this phenomenon H. Scholz [3] to use the so-called solid-on-solid (SOS) model: let the (001) surface of a simple cubic crystal. In general the energy U of the surface will depend on the different heights between sites.

In the nearest-neighbor approximation:

$$U = \gamma_0 A + \sum_{ij} [V(n_{i,j+1} - n_{ij}) + V(n_{i,j} - n_{ij})] \quad (5)$$

where γ_0 is the surface energy of the perfect (001) surface, A is the area, (i, j) labels the x - and y -directions (z - is the vertical direction), n_{ij} is the height of the column (the z coordinate) respect to arbitrary origin. V is the result of broken lateral bonds, then monotonically increasing. The common approximations are

$$V(n) = J |n| \quad (6)$$

no interaction between steps and the “discrete Gaussian model”

$$V(n) = J n^2 \quad (7)$$

Note that the SOS model does not take into account overhangs and quantum effects. Minimizing U gives $n_{ij} = n_0$ for $T = 0$, i.e. a perfect flat surface. At finite temperatures the free energy can be written as

$$F = U - TS = \frac{L}{a} [J - T \ln(n)] \quad (8)$$

where L is the length of a closed loop or step with height $n_{ij} = n' \pm 1$, a is the lattice constant. $S = \frac{L}{a} T \ln(n)$ the entropy of configuration which can be adopted in two dimensions by a line of length L and composed of $\frac{L}{a}$ segments [3] [5]. What can learn is that above the “roughening temperature” $T_R = \frac{J}{k_B m}$ it is favorable to have steps of arbitrary length, i.e. the crystal surface is invaded by fluctuating steps and becomes rough [5]. By considering the gaussian model and the derivation of Kosterlitz and Thouless one finds a very weak singularity of the free energy at the roughening temperature [3]

$$F_{\text{lim}} \propto \exp \left[\frac{-c}{|T - T_R|} \right], \quad c > 0 \quad (9)$$

Near T_R the correlation length diverges as

$$\xi(T) \propto \exp \left[\frac{c'}{(T_R - T)^{1/2}} \right], \quad c' > 0 \quad (10)$$

The fluctuations of the surface position are given by:

$$G(r) = \langle (n_{i,j} - n_{\infty})^2 \rangle, \quad r = a(i, j) \quad (11)$$

$$\propto \ln |\xi(T)| \quad \text{for } r \rightarrow \infty \quad (12)$$

$$\propto |T_R - T|^{-1/2} \quad \text{near } T_R \quad (13)$$

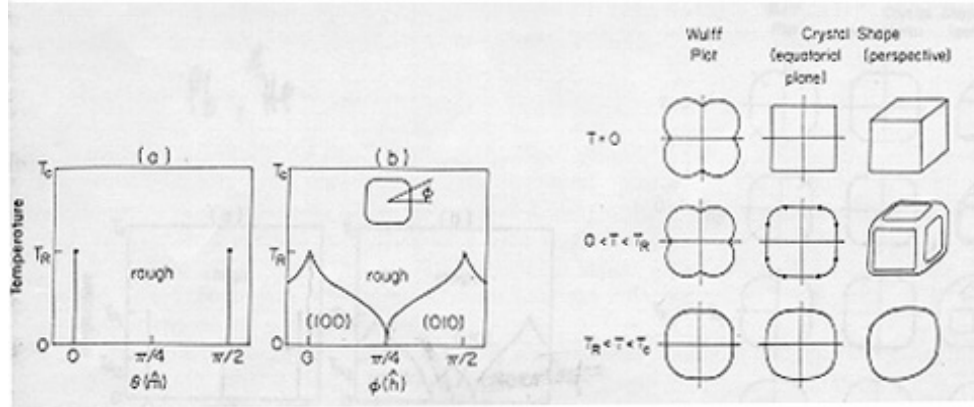


Figure 3: Interfacial phase diagrams for simple-cubic nearest-neighbor lattice-gas model. θ and ϕ are angular variables in an equatorial section of the three-dimensional phase diagram. It is also presented the Wulff plots and crystal shapes.

Thus the fluctuations remain finite below T_R , i.e. the surface is *macroscopically flat* (despite of local fluctuations). Above T_R ($\xi = \infty$), the fluctuations average out the discreteness of the $n_{i,j}$ -variables if long-distance correlations are considered.

Now using the gaussian potential

$$G(r) = \frac{1}{2\pi} \frac{T}{J_{eff}} \ln(r) \quad \text{for } r \rightarrow \infty \quad (14)$$

where $J_{eff} = \frac{1}{4}\pi T_R - O(|T - T_R|^{1/2})$ takes a universal value. Fluctuations in surface position diverge, so that there are no correlations between far away points, the surface is *macroscopically rough*. The Kosterlitz-Thouless renormalization group does not permit a determination of T_R in terms of J . However, Monte-Carlo calculations have found $T_R/J = 1.24$ and 1.46 for the potentials (6) and (7) respectively.

Finally, it is important to take a look at the thermodynamic phase diagram of the simple-cubic nearest-neighbor (Ising) lattice. in $d = 3$, they show the loci of singularities of the free energy in the space of its natural variables.[1]

The critical surface is always smooth or rough for $T > 0$. Fig (b) is the crystal face diagram. The roughening starts for $T > 0$ and in planes away of symmetry directions.

3.1 Quantum Roughening

Here I will address briefly the issue of the existence or absence of quantum roughening base on the work of A. Andreev *et. al.*[6] and S. Fisher *et. al.*[7] Andreev argues that the classical ECS theory predicts for ^4He crystals an atomically rough surface at $T = 0$ because of the transition entropy between the phases is very small and this fact can only be explained using quantum mechanical fluctuations at this temperature. They argue that the quantum motion can delocalize the kinks on the steps, and this leads for all crystalline planes to a negative energy for isolated steps and a finite number of them at $T = 0$. Then an atomically smooth surface of the crystal is unstable respect to step creation, i.e. superatomic steps are impossible and the surface energy is a smooth function of the orientation. Thus, these zero-point steps are responsible of a “quantum roughness” of the interface. This explanation agreed with what was known experimentally at that time (~ 1980).[6],[10]

On the other hand, Fisher and Weeks thought that Andreev's arguments were wrong and gave a lower bound for T_R :

$$T_R = (2d^2/\pi) |\bar{\gamma}_s - \bar{\gamma}_p|^{1/2} \quad (15)$$

where d is the step height and $|\bar{\gamma}_s - \bar{\gamma}_p|^{1/2}$ a mean value of the surface tension $\bar{\gamma}$. Fisher and Weeks say the energy per unit length considered by Andreev of a microscopic step is ill defined and not in general equal to the macroscopically defined step free energy. A smooth interface may consist of a large number of localized steps and islands, even at $T = 0$, but the properly defined macroscopic step free energy can still be nonzero.[3],[see 8]

4 Experiments

4.1 The solid-liquid ^4He Interface

As I mentioned before Andreev and Parshin [6] predicted that the interface between hcp ^4He crystals and superfluid ^4He has to be rough (absence of faceting) down to $T = 0$ as a consequence of the zero point motion of the atoms, the existence of melting freezing waves and anomalous reflection of sound waves and the discovery of roughening transitions. For crystals greater than the capillarity length ($l \sim 1.5 \text{ nm}$), the interface contains a large nearly horizontal portion and is bend near the walls. This surface is rough except near high symmetry axis where a roughening transition can occur. By 1980 was discovered the appearance of facets in two of the highest symmetry directions of the crystal around 1 K. Andreev's arguments, was thought, could be still applied to all other directions. However Balibar *et. al.* [9] found the existence of a third kind of facets on growth shapes below 0.35 K. At the same time, Weeks and Fisher suggested that Andreev's arguments were wrong.

I will describe the results of Balibar *et. al.*'s experiment. At 0.4 K the crystal contains (0001) or c planes perpendicular to the six fold symmetry axis and

planes which are parallel to this axis and could be either $(10\bar{1}0)$ or $(11\bar{2}0)$ type planes. These planes appear at $T_{R1} = 1.2 \pm 0.1$ K for growth and $T_{R2} = 0.9 \pm 0.1$ K for equilibrium shape in agreement with previous measurements. The new, so called "s", facet is present at 0.35 K for growth, makes an angle of $60 \pm 3^\circ$ with the c plane and can be either of $(10\bar{1}1)$ type if the facets are $(10\bar{1}0)$ or $(11\bar{2}2)$ type if the facets are $(11\bar{2}0)$. No other facets were observed down to 70 mK. To make sure that this is a roughening transition facets should be seen on equilibrium shape Balibar showed that there is no observable difference between the temperature at "s" facets appear on equilibrium shapes and growth shapes respectively. They measured $T_{R3} = 0.365 \pm 0.03$ K.

They used a transparent box closed at the bottom by a thin plate in which a small hole ($r = 0.8$ mm) was drilled (Fig. 4). A bubble forms in the hole whose equilibrium shape depends on the pressure difference across the interface and the surface tension. The pressure difference across this single crystalline bubble is obtained by measuring the height h_1 of the interface outside the box with the usual relation

$$\Delta P = \Delta \rho g h_1 \quad (16)$$

The height h_p of the bubble is a function of ΔP , and, at constant ΔP and for some orientation, it was observed to change at the various roughening transitions, a property useful to measure the various T_R at thermodynamic equilibrium.

The height h_p takes a high or a low value depending on whether the temperature is higher or lower than $T_{R3} = 0.365 \pm 0.3$ K. Wolf *et. al.*[10] suggests that these low values correspond probably to metastable shapes with at least one s facet anchored at some place in the lower part of the hole edge. When T increases up to T_{R3} , the s facets shrink, and since rough surfaces do not anchor on walls, the bubble moves at $T \sim T_{R3}$ toward an equilibrium position with a higher h_p . Values taken when $T \sim T_{R3}$ are not at equilibrium but measured during observed slow motion of the interface in a few minutes. Finally when the crystal is cooled down through T_{R3} , h_p keeps at high values probably because of the small size of the crystal shape and no anchoring reappears.

The table below compares the hierarchy of distances between planes in the hcp structure and the actual hierarchy of T_R found here.

T_R (K)	$T_{R1} = 1.2 \pm 0.1$	$T_{R2} = 0.9 \pm 0.1$	$T_{R3} = 0.365 \pm 0.03$
corresponding face	(0001)	$(00\bar{1}0)$ or $(11\bar{2}0)$	$(10\bar{1}1)$ or $(11\bar{2}2)$
angle with (0001)	0	90° 90°	58.5° 62.1°
na^2 or $d\sqrt{2}/a$	1.155	0.612 0.707	0.541 0.603
max step height d^*/a	0.816	0.577 0.5	0.637 0.426
$n/n_1 = d/d_1$	1	0.53 0.612	0.468 0.522
d^*/d_1^*	1	0.707 0.612	0.78 0.522
$(d/d_1)^2$	1	0.28 0.374	0.219 0.272
T_R/T_{R1}	1	0.9 ± 0.1	0.365 ± 0.03

Hierarchy observed of roughening transition.

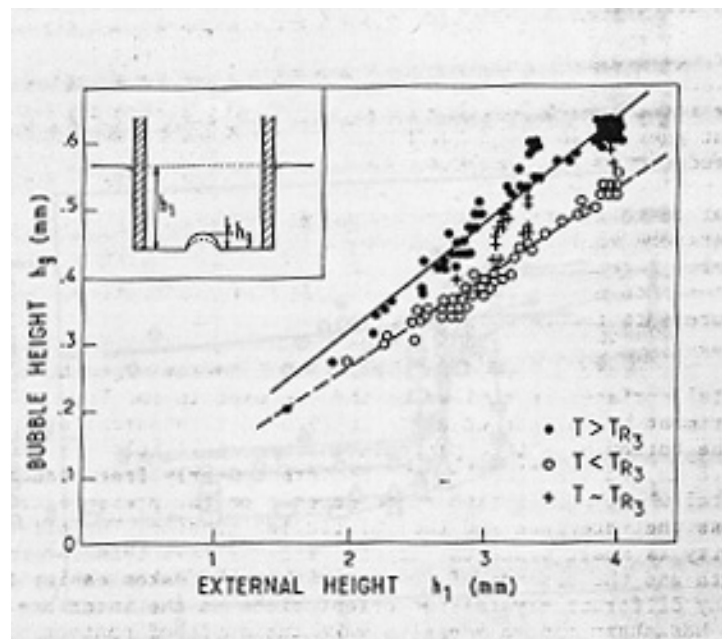


Figure 4: The variation of the height h_b of the crystalline bubble with height h_1 of the level outside the transparent box. Open circles correspond to temperatures $T < 0.34$ K and black circles to $T > 0.38$ K; crosses correspond to $T \approx T_{R3} = 0.365$ K. The solid and broken lines are guides to the eye.

where d^* is the maximum height of actual microscopic steps ($d^* \neq d$ because parallel planes are not always equidistant).

Are there others T_R ? To find this out, Balibar *et. al.* [9] estimates the various T_R approximately. T_R is roughly proportional to the step energy E_s and E_s is proportional to $\gamma_s \pi$ or $\gamma_s d$, where π is the surface density in the planes parallel to the facet under consideration and d their mean spacing. Given the fact that γ_s varies only with a factor two with orientation, they show that T_R is proportional to d . d^* also appears proportional to the density obtained by Drescher [9] who allows for some surface relaxation. Furthermore, the ratios presented are in qualitative agreement with the hierarchy of T_R , which implies that Weeks and Fisher [7] could be right, i.e, going down to lower temperature should show the appearance of more and more facets in an infinite surface.

The agreement between the experimental hierarchy and the various estimates made without quantum effect is qualitative, although out of the five planes shown to have similar densities, only three have been observed in this experiment. There is no explanation of this effect. On the other hand quantum motion seems necessary to interpret the very high mobilities observed for rough surfaces. [10]

Balibar *et. al.* [9] [10] concludes by pointing out that theoretical work is needed to compare the three different experimental values T_{R1} , T_{R2} , T_{R3} with calculations. This this will tell us the exact nature of zero point motion in the problem of roughening at the surface of Helium crystals.

4.2 Observation of pokrovsky-talapov critical behavior in lead crystals

Rottman *et. al.* [11] presents observations of a lead crystal critical exponent. They focus on the regime where facets and curved regions meet at edges, which may be either sharp (slope discontinuity) or smooth (no slope discontinuity). The smooth edge varies as [see Fig. 5]

$$y = A(x - x_c)^\theta + \text{higher-order terms} \quad (17)$$

where θ is a critical exponent. Mean field theory gives

$$\theta_{MF} = 2 \quad (18)$$

Calculation which include fluctuations predict

$$\theta_{theory} = \frac{3}{2} \quad (19)$$

This value is characteristic of the so-called Pokrovsky-Talapov [13] (or Gimben-Mullins) universality class and should be independent of temperature and facet orientation, provided $T < T_R(\hat{n})$.

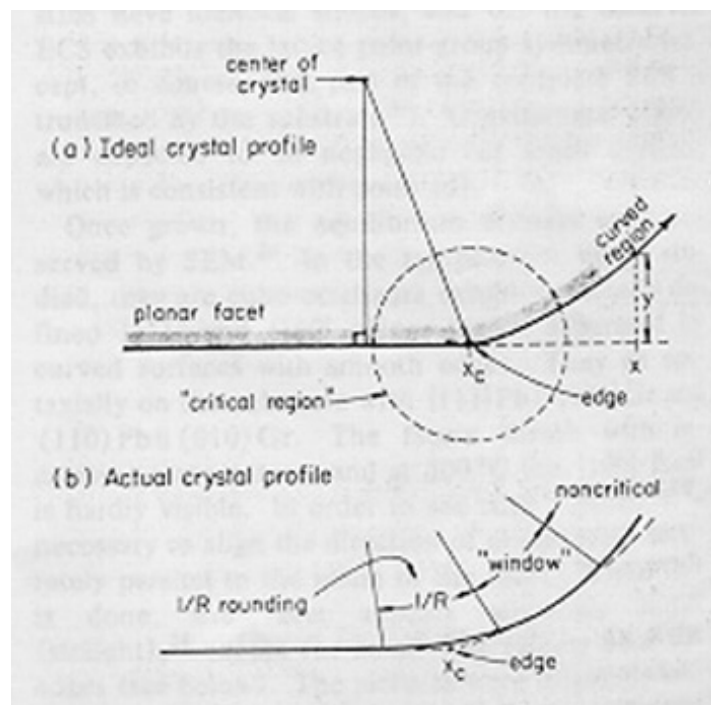


Figure 5: (a) ideal (b) actual crystal profiles through a smooth edge. The edge is rounded, x_c becomes a fit parameter, and only data from the window can be used.

Rottman *et. al.* [11] reports direct measurements of the exponent θ using scanning electron microscopy (SEM) of 2-10 μm Pb crystals grown on a graphite substrate. It is found values of θ which agrees with (8?) and not with mean field prediction providing a connection between surface phase transitions and equilibrium crystal shapes

From ECS we learn that sharp edges in on the crystal shape correspond to first-order phase transitions and smooth edges correspond to second order phase transitions. Thus, near the smooth edge of the lead crystals there is critical behavior. The value $\theta = \frac{2}{3}$ is based on (i) the interface can be modeled as a 2-dimensional surface, provided the bulk correlation length is small, and (ii) the dominant excitations of this surface are “steps” or “ledges”. [13]

The experimental method is described in Rottman *et. al.*[11] What it is also important is to confirm that the final forms attain are, indeed, equilibrium crystal shapes. This is so because (i) the shapes do not evolve in time; (ii) no matter which temperatures the crystals went through the shape is the same; (iii) crystals of different sizes have identical shapes; (iv) the ECS shows the lattice point-group symmetry. Gravitational effects are negligible for small crystals.

The crystals are cubo-octahedra exhibiting defined $\{111\}$ and $\{100\}$ planar facets, separated by curved surfaces with smooth edges. The facets shrink at 300°C approximately. The raw data is provided by enlarging of the SEM picture which was digitized. The angular range covers $\pm 18^\circ$ about the edge. Data points far from the edge cannot be expected to be fitted by the form of eq. (17) because corrections to scaling become important. Likewise very close data cannot be fitted too because of $1/R$ corrections due to the atomic-scale rounding of the ideally singular edge structure.

The value Rottman *et. al.* got with their best crystal and using a three-parameter (A, μ, θ) least-squares fit was

$$\theta = 1.60 \pm 0.15 \quad (20)$$

which is consistent with theory and other crystals and annealing temperatures.

5 Conclusions

Several issues have addressed in the present work. For example, that the equilibrium shape of a crystal is itself the free energy and any singularity on it determines the type of transition between the solid and fluid phase. It should be pointed out that the very existence of facets lays on the anisotropy of, at least, one of the two phases who share the interface. Facets characterizes crystal shapes as well as steps and kinks. The interaction between them gives the equilibrium crystal shape. Theoretically steps on a crystal surface may be considered solitons, i.e. topological objects which owes to the periodicity of the crystal, e.g. solutions of a sine-Gordon equation. There also several models to study the singularities that arises on the crystal shape amongst them the

solid-on-solid model gave a description of the critical behavior corresponding to the Kosterlitz-Thouless. However critical behavior is not constrained to one universality class. Experiments with lead crystals showed that the critical exponent is that of Pokrovsky-Talapov critical behavior [13]. There is experimental evidence against quantum roughening however the argument of Fisher lays on an infinite lattice. Fradkin concludes that the underlying periodicity of the crystal lattice always lead to flat faces at $T = 0$ together provided that quantum fluctuations of the surface do not diverge.

Many issues have been left out, however this paper was a stimulating work. I am grateful to Prof. N. Goldenfeld for his very useful suggestions.

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