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Equilibrium shape of crystals

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Résumé. — Nous décrivons les mécanismes physiques qui contrôlent la forme d'équilibre des cristaux. La transition rugueuse d'une face cristalline donnée est associée à l'annulation de l'énergie libre d'une marche sur cette surface. En dessous de la transition rugueuse, des facettes de taille finie coexistent avec des parties arrondies de la surface. Près du bord d'une facette, la forme du cristal est déterminée par l'interaction à longue portée entre les marches induite par les fluctuations. Une méthode de matrice de transfert simple conduit à la loi en puissance 3/2 de la forme du cristal en bord de facette (ce qui implique une divergence de la courbure) ainsi qu'à d'autres caractéristiques de la forme de la facette. Si les interactions à longue portée entre marches sont répulsives, des facettes d'ordre de plus en plus élevé peuvent se former à basse température conduisant à un « escalier du diable » à T = 0. Nous donnons les formules pour la largeur et la température de transition rugueuse des facettes d'indice élevé. Si les marches s'attirent, l'escalier du diable disparaît partiellement ou complètement et les coins entre différentes facettes peuvent rester stables à température non nulle.

Abstract. — The physical mechanisms governing the equilibrium shape of crystals are described. The roughening transition of a given crystal face is associated with the vanishing of the free energy of a step on that surface. Below the roughening transition, facets of finite size coexist with rounded parts of the surface. Near the boundary of a facet, the shape of the crystal is determined by a fluctuation-induced long-range interaction between steps. A simple transfer-matrix method is used to derive the 3/2-power-law for the crystal shape near the boundary (implying diverging curvature), as well as some other features of the facet shape. If there are long-range repulsive interactions between steps, facets of higher and higher order can form at low temperatures, leading to a devil's staircase at T = 0. Formulae for the width and roughening temperature of the high index facets are given. If there is attraction between steps, the devil's staircase disappears partly or completely, and edges between different facets can be stable at nonzero temperatures.

1. Introduction.

Generally, crystals are of polyhedral shape, the shapes of the faces and the angles of contact between them determined by symmetry and crystal structure. However, in a number of cases, equilibrium shapes are qualitatively different. For example, the equilibrium shape of 4He crystals is completely rounded above about 1.17 K, no flat facets exists. Below this temperature there appear facets on the crystals [1]. Up to now three different temperatures have been identified, below each of which a new type of facet is observed [2]. The appearance or vanishing of a given facet at a fixed temperature is associated with the so-called « roughening transition » of that facet. Related phenomena have also been observed in quite different systems and temperature ranges: (i) plastic crystals of C3Cl6 or NH4Cl show well defined facets only below approximately 100 °C [3], (ii) equilibrated crystallites of lead and gold exhibit both round parts and facets [4] (similar to 4He crystal shapes) at temperatures around 200 °C (Pb) and 1 000 °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 roughening [5], (iv) in colloidal crystals, no facets have been observed at all up to now, in marked contrast to « ordinary » crystals. The variety of experimental results is parallel by considerable theoretical interest in roughening and facet formation, and the relation to crystal growth [6-8].

In the present article I use some simple models to exhibit the underlying mechanisms. Chapter two recalls the mechanism and physical properties of the roughening transition of an infinite, low-index crystal
surface. Exhaustive reviews have been given by Weeks and collaborators [6]. In chapter three, facet formation on finite (but microscopic) crystals is discussed. A model for the thermal fluctuations of steps in the surface is described. The model allows a simple and quite general rederivation of exact results obtained previously by Jayaprakash et al. [7] for a specific case. In the fourth chapter, realistic long-range interactions on surfaces are considered, and the possibility of a « devil’s staircase »[9], involving surfaces or arbitrary high Miller indices, is investigated. All the considerations apply to thermal equilibrium, non-equilibrium phenomena like dendritic growth shapes are not considered [10].

2. The roughening transition.

The idea that the surface of a crystal may exhibit a phase transition is originally due to Burton, Cabrera, and Frank [11]. In the last decade, the physics of this roughening transition has been investigated in detail by Weeks and collaborators [6]. The phenomenon can be understood using the so-called solid-on-solid (SOS) model: consider the (001) surface of a simple cubic crystal, local deviations from a perfect (001) structure are due either to additional adsorbed atoms or to atoms lacking in the top layers of the crystal. Generally, the energy $U$ of the surface will depend on the difference of the height of the surface between different sites. Including only nearest-neighbour interactions one has:

$$ U = \gamma_0 A + \sum_{i,j} \left( V(n_{i+1,j} - n_{ij}) + V(n_{ij+1} - n_{ij}) \right). $$

(1)

Here $\gamma_0$ is the surface tension of the perfect (001) surface, $A$ is its area, $(i,j)$ label columns of the simple cubic lattice in the $x$- and $y$-directions, and the integer $n_{ij}$ is the height of the column (i.e. the surface) at $(i,j)$, measured with respect to an arbitrary origin (Fig. 1a). The potential $V$ may be thought to be due to the broken lateral bonds of an extra adsorbed atom. $V(n)$ is monotonically increasing and normalized to $V(0) = 0$. Often used approximations are:

$$ V(n) = J \mid n \mid, \quad (2a) $$

and the « discrete Gaussian model »

$$ V(n) = Jn^2. \quad (2b) $$

Note that there are no overhangs in the model, which is expected to be a good approximation well below the bulk melting temperature.

Obviously, at zero temperature (and neglecting quantum effects), $U$ is minimized by $n_{ij} = n_0$, i.e. a perfect (001) surface. At finite temperatures, there will be steps in the surface, separating regions of $n_{ij} = n'$ from regions with $n_{ij} = n' \pm 1$, and obviously these steps have to form closed loops (Fig. 1b). The free energy of a simple loop of length $L$ is

$$ F = U - TS = \frac{L}{a} [J - T \ln (m)] \quad (3) $$

where $a$ is the lattice constant, $S$ is the entropy, and $m$ is the number of different positions a step can take going from one lattice site to the next (which is of course temperature dependent), so that $S = (L/a) \ln (m)$. From equation (3) one concludes that above the « roughening temperature » $T_R = J / \ln (m)$ it is favourable to have steps of arbitrary length. The above argument neglects completely the influence of interactions between steps. These effects can be taken into account noting that the discrete Gaussian model is related to the two-dimensional two-component Coulomb plasma via a duality transformation [12] (i.e. high temperatures in the discrete Gaussian model correspond to low temperatures in the Coulomb plasma and vice versa). The properties of the Coulomb plasma have been derived by Kosterlitz and Thouless [13] and the following discussion is largely based on their results. One finds a very weak singularity of the free energy at the roughening temperature:

$$ F_{\text{sing}} \propto \exp[-c/|T - T_R|^{1/2}], \quad c > 0. \quad (4) $$

Below $T_R$ the properties of the system can be described by replacing the discrete integer variable $n_{ij}$ by a continuously varying average $u_{ij}$ as long as phenomena
on length scales shorter than the correlation length \( \xi(T) \) are considered. On these length scales thermal fluctuation have «average out» the discreteness of the \( n_{ij} \), \( \xi(T) \) can be considered as the maximum diameter of a thermally excited loop. On length scales larger than \( \xi(T) \) there are essentially no fluctuations. Near \( T_R \) the correlation length diverges as

\[
\xi(T) \propto \exp[c/(T_R - T)^{1/2}], \quad c > 0.
\]  

From the above, the width of an infinite step crossing the surface from \( y = -\infty \) to \( y = \infty \) is equal to \( \xi(T) \), whereas its free energy per unit length varies as \( 1/\xi(T) \) and therefore vanishes at \( T_R \). One can also obtain the fluctuations of the surface position:

\[
G(\mathbf{r}) = \left( n_{ij} - n_{00} \right)^2, \quad \mathbf{r} = a(i, j)
\]

\[
\propto \ln(\xi(T)) \quad \text{for} \quad r \to \infty \quad \text{(6a)},
\]

\[
\propto [T_R - T]^{1/2} \quad \text{near} \quad T_R. \quad \text{(6b)}
\]

Thus the fluctuations remain finite below \( T_R \), e.g. the surface is macroscopically flat (even though there may be important local fluctuations of the surface position, especially near \( T_R \)).

Above \( T_R \) there are loops of arbitrarily large diameter (i.e. \( \xi = \infty \)). These fluctuations average out completely the discreteness of the \( n_{ij} \)-variables if long-distance correlations are considered. Consequently, the properties of the system are described by an effective energy functional:

\[
U_{\text{eff}} = \gamma_0 A + J_{\text{eff}} \sum_{ij} \left[ (n_{i+1,j} - n_{ij})^2 + (n_{i,j+1} - n_{ij})^2 \right],
\]

where the \( n_{ij} \) are now continuous variables and \( \gamma_0 \) is the macroscopic surface tension of the flat surface, containing all fluctuation effects. Near \( T_R \) one has:

\[
J_{\text{eff}} = \frac{1}{4} \pi T_R - 0([T - T_R]^{1/2}),
\]

i.e. at \( T_R \) the stiffness constant takes a universal value. From equation (7) one finds:

\[
G(\mathbf{r}) = \frac{1}{2 \pi J_{\text{eff}}} \ln(r) \quad \text{for} \quad r \to \infty,
\]

i.e. the fluctuations in surface position diverge for large distances, so that there are no correlations between far away points, the surface is macroscopically rough. Equation (7) allows also to calculate the energy of a tilted surface, and thus the angle dependent surface tension (Eq. (11) below): \( \gamma_0 + \gamma'_0 = 2 J_{\text{eff}}/a^2 \) (\( \gamma'_0 \) is the second derivative of \( \gamma \) with respect to azimuthal angle). Using equation (8) one finds in particular [14]

\[
T_R = \frac{2}{\pi} a^2 (\gamma_0 + \gamma'_0).
\]

This formula can be directly compared to experiment.

The Kosterlitz-Thouless renormalization group does not permit a determination of \( T_R \) in tems of the «bare parameter» \( J \) (Eqs. (2)), this being a strong-coupling problem. However from Monte-Carlo calculations [15] one finds \( T_R/J = 1.24 \) and 1.46 for the forms (2a) and (2b) of \( V \) respectively. Note however, that the experimentally accessible quantity is rather \( \gamma_0 + \gamma'_0 \) than \( J \).

The growth of crystals usually proceeds via adsorption of single atoms (or molecules) at steps in the surface. Above \( T_R \), there are steps of all lengths. One then finds a linear relation between growth rate \( R \) and \( \Delta \mu \), the chemical potential difference across the surface: \( R = (I/\Gamma) \Delta \mu \), with \( \Gamma \) going to a nonzero constant near \( T_R \) [16]. Below \( T_R \) one has only steps of finite length. Growth proceeds via nucleation, and one has \( R \propto \exp[-\text{const.}/\Delta \mu] \), which will usually be much slower than the linear growth above \( T_R \).

### 3. Faceting.

Generally, the shape of a crystal is determined by the minimum of the surface free energy at a given volume, i.e. one has to minimize

\[
\int dx \; dy \left[ f(\mathbf{h}) - 2 \lambda z(x, y) \right], \quad \mathbf{h} = \nabla z(x, y).
\]

Here \( z(x, y) \) is the position of the surface, \( \lambda \) is a Lagrange multiplier introduced to satisfy the constant volume constraint, \( f(\mathbf{h}) \) is the surface free energy density, which is related to the angle dependent surface tension by

\[
f(\mathbf{h}) = \gamma(\theta, \phi) [1 + \mathbf{h}^2]^{1/2},
\]

and \( \theta, \phi \) are the polar angles of the surface normal. A first integral of the Euler equations of the variational problem is

\[
z - h_1 x - h_2 y = \frac{1}{\lambda} f(\mathbf{h}), \quad \mathbf{h} = (h_1, h_2).
\]

Setting \( \mathbf{h} = \nabla z(x_0, y_0) \), this is the equation of the plane tangent to the crystal at \( (x_0, y_0, z(x_0, y_0)) \). The distance of this plane from the origin is

\[
r = \frac{1}{\lambda} [1 + \mathbf{h}^2]^{1/2} = \frac{1}{\lambda} \gamma(\theta, \phi).
\]

This is the Wulff construction [17]: draw the polar diagram of \( \gamma(\theta, \phi) \). Then the crystal shape is given by the interior of all the planes tangent to this polar diagram. If \( \gamma(\theta, \phi) \) and its first derivative are continuous, one obtains smooth, rounded shapes. On the other hand, a break in the slope of \( \gamma \) will generally lead to flat pats, i.e. facets, in the crystal shape. The linear dimensions of these facets are proportional to the break in \( \gamma' \) [18]. The Wulff construction can be inverted to obtain \( \gamma(\theta, \phi) \) from experimental crystal shapes [4].
By a Legendre transformation on equation (12) one finds the explicit form of $z$ [19]:

$$
\lambda z(x, y) = g(-\lambda x, -\lambda y), \quad g(\eta) = \min_{h} \left[ f(h) - \eta h \right],
$$

(14)

which will be used in the following. $\eta$ can be thought of as a "tilt field", favouring an inclined surface with respect to a flat one. Of course, there is a stability criterion: $\partial^2 f / \partial h \partial h(\mu, \nu = 1, 2)$ should be a positive definite matrix. If there is one negative eigenvalue one will find an edge in the crystal, two degenerate negative eigenvalues lead to a conical point [8, 19].

Applying equation (14) to the model (1), (2b) one has (at $T = 0$) to minimize

$$
U = \gamma_0 A + J \sum_{ij} \left( \left( n_{i+1,j} - n_{ij} - \frac{1}{2} \eta_1 \right)^2 + \left( n_{i,j+1} - n_{ij} - \frac{1}{2} \eta_2 \right)^2 - \frac{1}{4} \eta^2 \right) (\eta' = \alpha^2 \eta / J),
$$

(15)

Obviously, a nonzero $\eta$ favours a surface with finite slope. On the other hand, the $n_{ij}$ are integers, so that in the absence of any further-neighbour interaction (see chap. 4) only a few simple surfaces minimize $U$. For example, looking at $z(x, 0)$, one has $\eta_2 = 0$ and therefore $n_{i,j+1} - n_{ij} \equiv 0$. Then $U$ is minimized by

\begin{align*}
&n_{i+1,j} - n_{ij} = 0 \quad \text{for} \quad |\eta_1| < 1 \\
&n_{i+1,j} - n_{ij} = 1 \quad \text{for} \quad 1 < |\eta_1| < 3 \\
&n_{i+1,j} - n_{ij} = 2 \quad \text{for} \quad 3 < |\eta_1| < 5, \text{ etc.}
\end{align*}

(16)

\[ \text{Fig. 2.} \quad \text{The } T = 0 \text{ crystal shape, obtained from the discrete Gaussian model with nearest neighbour interactions (Eq. (15)): (a) top view, (b) cut in the } x-z \text{ plane.} \]

\[ \text{Fig. 3.} \quad \text{Step configurations near the boundary of a facet: (a) steps with a kink (left), two touching (crossing) steps, a downstep: (b) schematic top view of the surface, showing approximately parallel, non-crossing steps.} \]

these kinks will allow the steps to wander around on the surface. On the other hand if the steps come together at one point one has $n_{i+1,j} - n_{ij} = 2$, requiring an extra energy of $2J$. Similarly, a "downstep" $(n_{i+1,j} - n_{ij} = -1)$ requires an extra energy $2J$. Consequently, these last two configurations are extremely unlikely at low temperatures, and the surface will look as figure 3b, with the steps fluctuating in position, but never touching nor returning. Obviously now the entropy of a configuration depends on the number of steps present, due to the more or less stringent steric constraints imposed on a given step by its neighbours. The problem of the statistical mechanics of the non-intersecting, non-returning steps can be solved noting that the trajectories of the steps in the $x$-$y$ plane are the same as those of one-dimensional spinless fermions in space-time, the Pauli principle taking care of the non-crossing condition [20].
The same situation occurs in the context of the commensurate (C)-incommensurate (IC) transition in two dimensions, the role of steps being played by domain walls between different commensurate regions. Much of the following has been taken over from work on the C-IC transition [21]. The partition function of the system described by $U$ (Eq. (15)) can be written

$$Z = \exp[-\beta g] \operatorname{Tr}(\hat{T}^{N_y}) , \quad \beta = 1/T ,$$

where $N_y$ is the number of horizontal rows and $\hat{T}$ is the row-to-row transfer matrix

$$\hat{T} = \exp(-\beta H) ,$$

$$H = J(1 - \eta_1^2) \sum_j a_j^+ a_j - T e^{-\beta J} \sum_j (e^{-\beta J a_j^+ a_j} + e^{\beta J a_j^+ a_j^+})$$

$= \sum_k (\mu - 2t \cos(k) - 2it' \sin(k)) a_k^+ a_k , (18c)$

with

$$a_j = \frac{1}{\sqrt{N_x}} \sum_k a_k e^{ikj} ,$$

$$\mu = J(1 - \eta_1^2) ,$$

$$t = T e^{-\beta J} \cos(\beta J \eta_2) , \quad t' = T e^{-\beta J} \sin(\beta J \eta_2) ,$$

and $N_x$ is the number of sites in the x-direction (i.e. $A = a^2 N_x N_y$). The $a_j(a_j^\dagger)$ in (18b) are fermion annihilation (creation) operators, one fermion corresponding to one step. The sites $j$ are now the possible positions of steps, and therefore are located half way between the original lattice sites. The first term in (18b) is the energy (per row) of the individual steps, whereas the second term describes the probability of a jump to the left or to the right. For $t \equiv 0$ these probabilities are different, and consequently one has a non-hermitian Hamiltonian in that case. One should note that the neglect of various processes discussed above (and others, see Schulz et al., ref. [20]) restricts the applicability of the transfer matrix to the region $e^{-\beta J} \ll 1$.

In the thermodynamic limit $N_y \to \infty$, the trace in equation (17) is dominated by the largest eigenvalue of $\hat{T}$, i.e. by the eigenvalue $E_0$ of $H$ with the smallest real part, and one has

$$g(\eta) = -\frac{T}{A} \ln (Z) = \gamma_0 + \frac{N_y}{A} E_0(\eta) .$$

$E_0$ is easily found from the diagonal form of $H$, equation (18c), by filling all $k$-states with negative real part of the eigenvalue. The imaginary part is odd in $k$, so that $\Im(E_0) = 0$, as expected. One finds two critical values of $\eta_1$ :

$$\eta_1^c = 1 \pm (T/J) e^{-\beta J} \cos(\beta J \eta_2) .$$

(21)

For $\eta_1 < \eta_1^c$, the fermion band is empty, $E_0 = 0$, there are no steps at all, corresponding to a (001) face. For $\eta_1 > \eta_1^c$, the band is completely filled, and $E_0 = N_x J(1 - \eta_1^2)$, there is one step per site, corresponding to a (010) face. On the other hand for $\eta_1^c < \eta_1 < \eta_1^c$, the band is filled up to the Fermi wave number $k_F = \cos^{-1}(\mu/2t)$, with

$$E_0 = \frac{N_x}{\pi} [\mu k_F - 2t \sin(k_F)]$$

$$\propto -N_x (\eta_1 - \eta_1^c)^{3/2} \quad \text{for} \quad \eta_1 > \eta_1^c .$$

(22)

In this region the mean distance $l$ between walls varies continuously with $\eta$ and therefore position (Eq. (14)), $l = \pi a/k_F$. This corresponds to a continuously curved surface. From equations (14), (20), (22) one finds near the edge of the (001) face, located at $(x_0, y_0, z_0)$

$$z_0 - z \propto [x_0(y_0) - x]^{3/2} ,$$

and a similar law near the edge of the (010) face. The power $3/2$ in equation (23) implies that the radius of curvature in the direction perpendicular to the edge vanishes as $R \propto [x_0(y_0) - x]^{1/2}$. In the context of the C-IC transition the (001) and (010) facets correspond to C phases: the step density does not vary with the parameter $\eta$. On the other hand, on the rounded parts of the crystal surface, the step density varies continuously with $\eta$, equivalent to an IC phase.

The shape of a facet is given by the critical curve $\eta_1^c(\eta_2^c)$, however, the form given by equation (21) is only correct if $\eta_2^c < \eta_1^c$, otherwise other excitations would have to be included in the transfer matrix. A qualitative sketch of the facet shape is given in figure 4. Note that the width of the round parts grows like $(T/J) e^{-\beta J}$ at low temperatures.

Inverting the Legendre transformations, equation (14), the free energy of the surface at given $h$ is

$$F(h) = A \left[ \gamma_0 + (J - 2t) \frac{1}{a} + \frac{2\pi^2}{3} \frac{a}{l^3} + 0(l^{-4}) \right] ,$$

$$|h| = \frac{a}{l} .$$

(24)

The $1/l$-term is just the free energy of a single step, whereas the $l^{-3}$-term is an effective repulsive long-range step-step interaction, induced by the thermal
fluctuations in step position (note that this term vanishes for $T \to 0$). This interaction can be explained by the loss of entropy \[22\] (i.e. increase in free energy) imposed by the « non-crossing » condition. The above considerations were made specifically for the case $\eta_1 \approx 1$, so that up-steps $(n_{i+1,j} - n_{ij} = 1)$ are the relevant excitations. Exactly analogous arguments apply near $\eta_1 \approx -1$, when down-steps $(n_{i+1,j} - n_{ij} = -1)$ are considered. In particular, one then finds $F(h) = F(-h)$. The linear term in $1/l$ in equation (24) implies a cusp in $F(h)$ (or equivalently in $\gamma(0, \phi)$), and therefore, from the Wulff construction, a finite (flat) facet. In the rounded parts of the surface, one may write

\[ n_{ij} = \langle \nabla n \rangle(x, y) + u(x, y) , \quad (25) \]

where $\nabla$ is the discrete gradient operator, and $(x, y) = a(i, j)$. The long wavelength ($> l$) variations of the fluctuation $u$ are continuous, due to the thermal step wandering, and can be shown to be governed by an effective energy functional \[23\]

\[ U_{\text{eff}} = \frac{1}{2} \int d^2r \left( K_x \left( \frac{\partial u}{\partial x} \right)^2 + K_y \left( \frac{\partial u}{\partial y} \right)^2 \right) , \]

\[ K_x = 2 \pi T \sin (k_F) e^{-\beta \eta_0} \cosh (\beta J \eta_1) , \quad (26) \]

\[ K_y = \frac{\pi J \eta_2^2 e^{\beta J}}{2 \sin (k_F) \sinh (\beta J \eta_1)} . \]

One remarks the strong anisotropy in the coefficients $K_x$, $K_y$ near the edges of the facets ($k_F \to 0, \pi\)$ \[24\]. This is due to the finite stiffness of individual steps (governing $K_x$) and the simultaneous vanishing of the interaction between steps (governing $K_y$).

Equation (26) leads to

\[ \langle [u(r) - u(0)]^2 \rangle = \frac{T}{\pi \sqrt{K_x K_y}} \ln (r) \quad \text{for} \quad r > l , \quad (27) \]

i.e. there are diverging fluctuations, compare equation (9), on the rough parts of the surface. Thus « rough » and « rounded » are actually synonymous.

Up to here, the discussion of this chapter was restricted to low temperatures ($e^{-\beta \eta} \ll 1$). On the other hand, near $T_R$ the long correlation length averages out details of the lattice structure, and then the free energy of a single step is expected to be independent of its orientation with respect to the lattice. From chapter 2 the free energy per unit length of a step varies as $f_{\text{step}} \propto 1/\xi(T)$, and equation (14) gives, to lowest order in step density

\[ g(\eta) = \gamma_0 + \min_i \left( \frac{1}{T} (f_{\text{step}} - | \eta | | a \right) . \quad (28) \]

Thus the (001) face is stable for $| \eta | a < f_{\text{step}}$, giving for the radius $\rho$ of the facet near $T_R$

\[ \rho \propto 1/\xi(T) \propto \exp[-c/(T_R - T)^{1/2}] . \quad (29) \]

Thus the facet disappears at the roughening transition, and this is actually the experimentally used criterion for determining the existence and temperature of a roughening transition \[1-3\]. From the work on the C-IC transition \[21\] one concludes that the power law, equation (23), holds at all temperatures in the vicinity of a facet. An argument based on equation (28) can actually be used to determine the facet shape at all temperatures, however then the angular dependence of $f_{\text{step}}$ has to be taken into account.

Above $T_R$, using equations (7) and (14) one finds

\[ \lambda z(x, y) = \gamma_0 - \frac{a^2}{4 \gamma_{\text{eff}}} r^2 + C_1 (\lambda r)^{s(T/\gamma_{\text{eff}})} r^{-2} \quad (30) \]

where the last, nonanalytic term is obtained from an analogous calculation on the C-IC transition \[25\]. From the universal value of $\gamma_{\text{eff}}$ at $T_R$ one finds for $T \to T_R$ from above

\[ z(0, 0)/R_c = \frac{2}{\pi} a^2 \gamma_0 / \xi(T_R) , \quad (31) \]

where $R_c$ is the crystal radius of curvature at $(0, 0, z(0, 0))$. Thus there is a universal jump in surface curvature \[7\] at $T_R$, associated with the jump of $\gamma_{\text{eff}}$. Note that this relation involves $\gamma_0$ only, whereas the other universal relation, equation (10), contains the combination $\gamma_0 + \gamma_0^*$. Many of the results obtained above from semi-quantitative arguments have originally been derived from a special type of SOS model, the so-called body centred solid-on-solid (BCSOS) model \[20\], by Jayaprakash et al. \[7\]. This model is adapted to the specific structure of the (100) face of a bcc crystal, and it is equivalent to the exactly solved six-vertex model \[27, 28\]. Specifically, the shape of the (100) facet can be obtained at all temperatures. The results are in complete agreement with the above discussion : (i) the temperature dependence of the facet diameter near $T_R$, equation (29), is confirmed, (ii)
the jump in curvature, equation (31), is verified, (iii) the 3/2-power law, equation (23), is recovered, (iv) the width of the round parts varies as $T e^{-c_{\text{const.}}/T}$ at low $T$ both in the BCSOS model and in our above fermion calculation (cf. Eq. (21)), (v) the nonanalytic term in equation (30) can also be found in the six-vertex model [25]. 

On the other hand, mean field theory [19] gives quite different results: (i) $p \propto (T_{c} - T)^{1/2}$, (ii) $1/R_c \propto T - T_{c}$, and (iii) $z_0 - z \propto (x - x_0)^2$ near a facet boundary. This failure of mean-field theory emphasizes the importance of fluctuation effects, both of the roughening transition and near facet boundaries (i.e. the fluctuation induced $1/l^2$ interaction between steps).

### 4. Long range interactions between steps.

The model discussed in the preceding chapter only includes a on-site repulsive interaction between steps, and the same is true for the BCSOS model. To investigate the effects of more general interactions, we first generalize the discrete Gaussian model (Eqs. (1), (2b)) so as to include nearest-neighbour interactions along the $x$-axis.

$$H = (a_{10} + 4 a_{20}) (1 + \eta'_1) \sum_j a^+_j a_j + 2 a_{20} \sum_j \left( a^+_j a_j - \frac{1}{2} \right) \left( a^+_{j+1} a_{j+1} - \frac{1}{2} \right) - T e^{-\beta a_{10}} \sum_j \left( e^{-\beta a_{10} a_j} a^+_j a_j + e^{\beta a_{10} a_j} a^+_j a_{j+1} \right) - \frac{1}{2} a_{20} N_x,$$

$$\eta'_1 = a^2 \eta_1/(a_{10} + 4 a_{20}), \quad \eta'_2 = a^2 \eta_2/a_{10}.$$  \hfill (33)

For $\eta_2 = 0$, i.e. $y = 0$, this Hamiltonian is equivalent, via the Jordan-Wigner transformation [29], to the exactly solved XXZ spin chain problem [30]. From this analysis one finds: (i) for $a_{20} > 0$, corresponding to the antiferromagnetic spin chain, there is a roughening transition of the (102) face at $\eta'_1 = -1$, with $T_R$ given by

$$T_R e^{-a_{10}/T_R} = a_{20}.$$  \hfill (34)

Below $T_R$, the crystal shape has the characteristic properties discussed in chapter 3, including the $z - z_0 \propto (x - x_0)^{3/2}$ law. The temperature dependence of the linear dimension of the (001), (102), and (101) facets is shown schematically in figure 5a. Note that this is not a phase diagram: the only point where there exist thermodynamic singularities is the roughening transition of the (102) facet. (ii) For $a_{20} < 0$, corresponding to the ferromagnetic chain, the (001)-(101) edge is stable up to a critical temperature $T_c$ given by

$$T_c e^{-a_{10}/T_c} = -a_{20}.$$  \hfill (35)

Only above this temperature is the entropy of fluctuating steps large enough to overcome the attraction and to form a rough, rounded part of the crystal surface (Fig. 5b). Note that the initial slope of the facet boundaries is finite. Denoting the boundary of the (001) facet by $x_0(T)$ one has

$$x_0(T_c) - x_0(T) \propto T e^{-a_{10}/T} + a_{20}, \quad (T \gtrsim T_c).$$  \hfill (36)

For $\eta'_2 \neq 0$ (i.e. $y \neq 0$) the model, equation (33) corresponds to a spin chain with an imaginary Dzyaloshinskii-Moriya interaction [31]. Though this has not yet been solved, one should note that it is closely related to a six-vertex model in a nonzero horizontal electric field, which has been solved [27]. It is thus very likely that an exact solution of $H$, equation (33) can also be found for $\eta'_2 \neq 0$, which would give additional information on the shape of the (102) face in that model.

Interactions between steps in real systems are certainly of longer range than just nearest neighbour.
Fig. 5. — Facet size (along x) as a function of temperature for the model described by equation (32) for (a) repulsive and (b) attractive step-step interaction. In (b) an edge is stable up to $T_c$. When longer-range repulsive interactions are included, more and more high-order facets appear at low temperatures, as indicated by the insert in (a). This occurs in a self-similar fashion, leading to a devil’s staircase at $T = 0$.

For example, the interaction potential $V(\lambda)$ between two steps a distance $\lambda$ apart, due to the elastic strains in the bulk solid, is [8]

$$ V(\lambda) \propto \lambda^{-2}. \quad (37) $$

If one considers the van der Waals interaction between atoms one finds [18]

$$ V(\lambda) \propto \lambda^{-3} \quad (38) $$

at large distances. In both these cases the interaction is repulsive (between steps of equal « sign »). On the other hand, in metals Friedel oscillations of the conduction electrons lead to oscillations of $V(\lambda)$, with period $k_F^{-1}$, so that the potential may well be attractive at certain distances.

To investigate the effect of long-range interactions consider the general model energy functional

$$ U = \gamma_0 A + \sum_{\langle im \rangle} a_{im} (n_{i+1,j+m} - n_{ij})^2, \quad (39) $$

where the cubic symmetry imposes $a_{im} = a_{i,-m} = a_{mi}$, $\langle im \rangle$ in equation (39) indicates summation over $l > 0$, $-\infty < m < \infty$ and $l = 0$, $m > 0$.

The energy of a single step parallel to the $y$-direction is

$$ E_1 = N_y \sum_{\langle im \rangle} l a_{im}, \quad (40) $$

and the interaction potential between two such steps is

$$ V(\lambda) = 2 N_y \sum_{l>\lambda} (l - \lambda) a_{im}. \quad (41) $$

Thus the discrete second derivative of $V$ is

$$ V''(\lambda) = V(\lambda + 1) - 2 V(\lambda) + V(\lambda - 1) = 2 N_y \sum_{m} a_{im}, \quad (42) $$

i.e. if all $a_{im}$ are positive, $V$ is repulsive and convex.

As demonstrated in the beginning of this chapter, introducing longer-range interaction may lead to the appearance of new, high index facets. To investigate this possibility, one has to minimize (cf. Eq. (14)):

$$ G = U - a^2 \left[ \eta_1 \sum_{ij} (n_{i+1,j} - n_{ij}) + \eta_2 \sum_{ij} (n_{i,j+1} - n_{ij}) \right]. \quad (43) $$

I first consider the case $y = 0$, i.e. $\eta_2 = 0$, and as a first step only « simple » faces with Miller index $(10p)$, i.e. there is one step $(y)$ every $p$ lattice constants (Fig. 6a). One easily finds

$$ G((10p)) = \frac{N_y}{P} \left[ E_1 (1 - \eta_1) + \sum_{l \geq 1} V(lP) \right], \quad (44) $$

where $\eta_1 = a^2 \eta_1 N_y/E_1$.

Fig. 6. — (a) Structure at some high-index face. (b) The devil’s staircase for repulsive, convex step-step interaction (along $y = 0$). Between each pair of faces, more higher-index faces exist, in a self similar way, as indicated by the insert. For clarity the extension of the (103), (203), and (104) facets is exaggerated.
The boundaries of a \((10p)\) facets are given by \(G((10p)) = G(10, p \pm 1)\), and one verifies that all \((10p)\) facets \((1 \leq p \leq \infty)\) exist in between the \((001)\) and \((101)\) facets provided that \(V''(\lambda) > 0\) for all \(\lambda\).

However, for large \(p\), the linear dimensions of a facet are

\[
\Delta x((10p)) \propto \eta_{1c}(p) - \eta_{1c}(p + 1) \propto p V''(p),
\]

and therefore become very small \(\left(p^{-3}\right)\) even for the relatively slowly decaying elastic interaction (Eq. (37)).

In concentrating on \((10p)\) facets I have obviously not accounted for the possibility of more complicated structures, e.g. (203) or (205). Generally, between a \((10p)\) and a \((1,0,p + 1)\) facets one expects facets with a periodic arrangement of steps either \(p\) or \(p + 1\) lattice constants apart. Such structures can be described by

\[
\theta(i) = 1 \text{ if } i \geq 0, \quad \theta(i) = 0 \text{ if } i < 0.
\]

The new variables \(\tilde{\eta}_m\) are the displacements of the \(m\)-th step from its position on a \((10p)\) facets. Inserting equation (46) into \(G\), equation (43) one finds (approximately [32])

\[
G = \gamma_0 A + \sum_{ij} \tilde{a}(\tilde{\eta}_{i+1} - \tilde{\eta}_i)^2 - \tilde{\eta} \sum_{ij} (\tilde{\eta}_{j+1} - \tilde{\eta}_j).
\]

This is of the same form as the original functional, however with renormalized coefficients, in particular one has

\[
\tilde{a}_i = \frac{1}{2} V''(lp).
\]

Using arguments analogous to those following equation (43) one can now determine the region of stability of all facets with Miller indices \((s, 0, sp \pm 1)\) with arbitrary \(s\). All these facets have a finite region of stability provided that the new \(V\) is repulsive and convex, which is the case if \(V\) satisfies these conditions (cf. Eqs. (42), (48)).

The above procedure is manifestly recursive, the new \(G\) (Eq. (47)) having the same functional form as the original one (Eq. (43)). This demonstrates the existence of a finite range of stability (in \(x\)) of all \((q0p)\) facets provided the original \(V(\lambda)\) is repulsive and convex everywhere. High index faces have, however, very narrow ranges of stability.

\[
\Delta x((q, 0, p)) \propto p V''(p) \quad (p, q \text{ relatively prime})
\]

and are squeezed in between low index faces, so as to form the so-called « devil's staircase » (Fig. 6b). Then, between any pair of facets, there is an infinite number of higher-index facets, and no finite angles of contact exist. However, most of the high-index facets have a vanishingly narrow range of stability (cf. Eq. (49)), and therefore they will be very hard to observe experimentally. The possibility of such a phenomena has been pointed out originally by Landau [18], and its existence has been proven for a one-dimensional model like equation (47) by Aubry [33].

The above considerations apply to a repulsive, concave \(V(\lambda)\). To understand the effect of deviations from this condition, replace \(a_{20} \rightarrow a_{20} - C\), so that for sufficiently large \(C\) there is a short-range attraction between walls. A positive \(C\) lowers the energy of the \((101)\) face with respect to all the other faces. Consequently, with increasing \(C\) beyond \(a_{20}\) more and more of the high index facets adjacent to \((101)\) will vanish, restricting the devil's staircase to an increasingly narrower range. Finally, if

\[
C > \frac{1}{2} \sum_{i \neq 1} V(i; C = 0)
\]

the devil's staircase disappears completely the \((001)\) and \((101)\) faces are in direct contact.

Constructing the \((101)\) face from steps in the \((001)\) face and explaining its stability in terms of interactions between these steps may seem a bit artificial, especially noting the inadequacy of the discrete Gaussian model for high-angle surfaces. One might rather construct a SOS-model directly for the \((101)\) face. Nevertheless, the above example demonstrates the stabilization of a given face by attractive step-step interactions and one easily sees that attractive interactions at longer range stabilize higher-index faces and may lead to finite angles of contact between them.

The roughening of high-index facets now occurs by thermal excitations of loops of « secondary steps » in the ordered array of steps (Fig. 7). On a \((q0p)\) facet,

\[
\text{the energy per unit length of such a secondary step is roughly } V''(p)/N_y.
\]

On the other hand, a secondary step may wander by creation of kinks with energy \(E_{kink} = \sum_m ma_{0m}\). Thus there is an extra free energy per lattice site due to the possibility of exciting these kinks:

\[
f_{kink} = -T \ln (1 + 2 e^{-E_{kink}/T}) \approx
\]

\[
\approx -2 T e^{-E_{kink}/T} (T \ll E_{kink}).
\]
The free energy of a single secondary step of length $L$ then follows as

$$F_{\text{step}} = L \left[ V'(p)/N_p - 2T e^{-E_{\text{kink}}/T} \right].$$  \hfill (52)

The roughening temperature of the $(q0p)$ facets is determined by the vanishing of this expression, i.e.

$$T_R = \frac{1}{2N_p} \frac{V''(p)}{e^{E_{\text{kink}}/T_R}}.$$  \hfill (53)

This is exactly the relation derived for the model treated at the beginning of this chapter (cf. Eq. (34)).

For $V'' \ll E_{\text{kink}}$ one finds

$$T_R \propto \frac{E_{\text{kink}}}{\ln \left| V''(p) \right|},$$  \hfill (54)

so that the roughening temperature decreases much slower with increasing $p$ than the width of the facet (cf. Eq. (45)). In a diagram like figure 5a the high index facets appear in between the low-index (001), (102), and (101) facets, in a self-similar fashion [34]. The position of the « spikes » of each facet is determined by the requirement that the free energies of an « up » step $(p \rightarrow p - 1)$ and a « down » step $(p \rightarrow p + 1)$, calculated from equation (43), be equal. The principal features of the facets below their roughening temperatures are those discussed in chapter 3. If there is attraction between steps, so that some facets meet at a finite angle, the behaviour is that of figure 5b.

Up to here, we have only considered facets with indices $(q0p)$, which occur for $y \approx 0$ (i.e. $\eta_2 = 0$) and by symmetry, also near $x = 0$ at arbitrary $y$. For the general case, one has to allow $\eta_2 \neq 0$ in equation (43), and this leads to the appearance of steps tilted away from the $y$-axis (Fig. 8a). The energy of a step with $N_k$ kinks at positions $\nu_1, \ldots, \nu_{N_k}$ is:

$$E_{\text{step}}(N_k) = E_{\text{step}}(0) + N_k E_{\text{kink}} +$$

$$+ 2 \sum_{\alpha < \beta} W(\beta - \alpha, \nu_\beta - \nu_\alpha),$$  \hfill (55)

with the kink-kink interaction

$$W(p, q) = 2 \sum_{m > q} (m - q) a_{pm}.$$  \hfill (56)

Provided this interaction is repulsive and convex, it can be shown (using similar methods as for Eq. (39)) that the structure minimizing $E_{\text{step}}(N_k)$ forms a devil's staircase. Consequently, denoting the boundary of the (001) facet by $y_0(x)$, the derivative $\partial y_0/\partial x$ will exhibit a devil's staircase structure similar to figure 6b. Of course, if there is attraction between kinks at certain distances, the devil's staircase will be partly or completely destroyed, and different parts of $y_0(x)$ will meet at finite angles.

The full shape $z(x, y)$, using a model like equation (39), is obviously a quite complicated problem, involving interactions between steps and kinks on different steps. However, for suitably repulsive and convex interactions a « two-dimensional devil's staircase », with faces of arbitrary high indices $(r, q, p)$ may be anticipated [35] (Fig. 8b). Contacts between facets at a finite angle will generally require some attraction between kinks or steps. Even though the roughening temperature of the high-index faces is expected to decrease quite slowly with increasing index, similar to the case of $(q0p)$ faces (Eq. (54)), their linear dimensions will decrease rapidly (cf. Eq. (45)), making this two-dimensional devil's staircase very hard to observe.

Finally one may note that nonanalyticities of the type of the last term in equation (30) are expected in the round part whenever the slope of the rough crystal surface passes through a rational value. This sequence of nonanalyticities is called a « floating » devil's staircase [25]. However, the nonanalyticities are quite weak ($\propto r^{4\pi T/Tr_0 - 2}$), especially if the slope corresponds to a high-index face, so that $T \gg T_R$, and will hardly be observable.

5. Summary and discussion.

In this article I have tried to summarize the basic physical mechanisms governing the equilibrium shape of crystals. Special emphasis has been put on the factors governing the respective size of faceted (flat) and rounded (rough) parts of the crystals surface.
The roughening transitions [6, 11] of a given crystal face is characterized by the vanishing of the free energy of a single step on that surface (cf. Fig. 7). Above the roughening temperature there are diverging (with sample size) fluctuations of the surface position, the surface is rough. Below $T_R$ the fluctuations remain finite (but may still be large, especially near $T_R$). In this sense the surface is macroscopically flat. The roughening transition is of the Kosterlitz-Thouless [13] type, characterized by an exponentially diverging correlation length and a universal jump in the surface tension.

The discussion given here implicitly assumes that the underlying crystal lattice is well ordered, i.e. that one is at temperatures well below the bulk critical (melting) temperature $T_c$. For a three-dimensional Ising model, using the $T_R$ obtained from the SOS model, one certainly has $T_R < T_c$. On the other hand, melting transitions are usually of first order and not adequately described by a simple Ising model. The relation between $T_c$ and $T_R$ in this case is not yet clarified.

The surface of a finite crystal is necessarily closed, and its precise shape is determined, *via* the Wulff construction, by the free energy in an « external field » $\eta$ which tends to tilt the surface away from its minimum energy configurations. Above $T_R$ the crystal shape is completely rounded, although, due to crystal anisotropy, not generally spherical. Below $T_R$, a finite energy (i.e. a finite $\eta$) is required to create a step and to tilt the surface. Consequently, there are flat parts, facets, below $T_R$. The faceted parts of the total crystals surfaces increase in size with decreasing temperature, at the expense of rounded parts. Near the boundary of a facet, the fluctuation induced long-range repulsion between steps leads to the characteristic $3/2$-power-law, equation (23). In addition fluctuations in the step positions on the rounded parts make these parts of the crystal surface macroscopically rough.

I have used a simple and quite general transfer-matrix method to demonstrate the above results which had been derived originally by Jayaprakash et al. [7] using a model for a specific surface. The formalism has been used previously in the context of the incommensurate (C) — incommensurate (IC) transition [20, 21] in two dimensions, flat and rounded parts corresponding to the C and IC phases respectively. However, the transition from a flat part to a round part of the crystal surface (at constant temperature) should not be considered as a phase transition: there are no singularities of the thermodynamic properties of the surface associated to it (the situation is of course quite different in the case of the C-IC transition). The only thermodynamic singularities occur at the roughening temperatures of different crystal faces.

Generally, interactions between steps on a surface will be of long-range. The interaction due to elastic strains in the bulk solid, for example, is repulsive and decays as $1/l^2$, where $l$ is the distance between steps. Such long-range repulsive interactions lead, at zero temperature, to the « devil's staircase » phenomena [9]: facets with arbitrary high rational Miller indices are stable, and there is an infinity of higher order facets in between each given pair of facets. This phenomenon has been demonstrated here for some simple cases. For the general crystal shape $z(x, y)$ a « two-dimensional devil's staircase » can occur [35]. It has been shown that the range of stability of the high order phases is extremely narrow, (Eq. (45)), making the devil's staircase quite difficult (if not impossible) to observe. On the other hand the roughening temperature is expected to decrease only slowly with increasing Miller index (Eq. (54)).

If there is attraction between steps part or all of the devil's staircase will disappear, and finite contact angles between different faces can be stable up to some nonzero temperature. This is quite similar to the so-called « harmless staircase » of C-IC transitions [36].

One should note that only facets with rational Miller indices appear. An « incommensurate » flat facet, with irrational Miller indices, would be destroyed at any nonzero temperature by the thermal wandering of the steps, due to the infinite degeneracy of an incommensurate ground state, and thus become rough. At zero temperature, the periodic underlying lattice will always lead to a commensurate structure.

The model I used in this paper applies directly only to the (001) and adjacent high index faces of a simple cubic crystal. However, the basic physical mechanisms, like the vanishing of the step free energy due to entropy, the fluctuation mediated $1/l^2$ interactions between steps, or the stabilization of high-index faces by step-step repulsion, are independent of the underlying lattice structure. I therefore expect that the main results discussed here apply qualitatively to arbitrary crystal faces and symmetries.

I did not discuss quantum effects. Originally it had been argued [37] that the energy gain due to the delocalization of kinks may bring down the energy of a step to zero, thus leading to « quantum roughening » at zero temperature. However, it can be shown quite generally that the quantum fluctuations of a surface do not diverge [14], and consequently the underlying periodicity of the crystal lattice will always lead to flat faces at $T = 0$ [38].

In principle, gravity may be thought to have important effects on roughening, in limiting the height fluctuations of the surface. Gravity will play a role on length scales larger than the « capillary length » [8] $A \approx [\gamma_0 + \gamma_\delta]/g(\rho_s - \rho_l)^{1/2}$, (g is the earth’s acceleration, $\rho_s$ and $\rho_l$ are the densities of the solid and the surrounding medium (« liquid »)). Generally, $A$ is of the order of some millimeters, so that in most practical cases gravity can be neglected.

Experimentally, roughening transitions occur in a number of systems, as mentioned in the introduction.
The most spectacular example certainly is $^4$He, where three different transitions, corresponding to three different faces, occur [1, 2], and the universal relations, equations (10) and (31), seem in fact to hold [39]. Concerning the possibility of a roughening transition of various copper faces [5], it is at first sight surprising that the roughening temperature decreases only very slowly with increasing Miller index. However, this finds a quite natural explanation: equations (53) and (54) actually predict only a weak index dependence of the roughening temperature.

A recent analysis [40] of the shape of lead crystalites confirms the 3/2-power-law for the crystal shape near the edge of a facet.

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