Wulff shape of equilibrium crystals

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The shape of an equilibrium crystal is obtained, according to the Gibbs thermodynamic principle, by minimizing the total surface free energy associated to the crystal-medium interface. To study the solution to this problem, known as the Wulff construction, is the object of the article.

Introduction

When a fluid is in contact with another fluid, or with a gas, a portion of the total free energy of the system is proportional to the area of the surface of contact, and to a coefficient, the surface tension, which is specific for each pair of substances. Equilibrium will accordingly be obtained when the free energy of the surfaces in contact is a minimum.

When one of the substances involved is anisotropic, such as a crystal, the contribution to the total free energy of each element of area depends on its orientation. The minimum surface free energy for a drop of a given volume determines then the ideal form of the crystal in equilibrium.

The principle of minimum free energy appears in the fundamental work of J.W. Gibbs, “On the equilibrium of heterogeneous substances” (1875-1878) where, in particular, he shows the role of the anisotropic surface tension for the determination of the shape of a crystal in equilibrium and discuss the formation of facets. He also points out the complexities of the actual crystal growth and suggest that only very small crystals can have an ideal equilibrium form.

G. Wulff, who made classical experiments on crystal growth, reported his results in the paper “Zur Frage der Geschwindigkeit des Wastums und der Auflösung der Kristallflächen” (1901), first published in russian in 1895. His principal conclusions include the celebrated Wulff’s theorem:

“The minimum surface energy for a given volume of a polyhedron will be achieved if the distances of its faces from one fixed point are proportional to their capillary constants.”
The term capillary constants was used for the surface tension. Wulff himself supported his principle mainly by its consequences and his attempt at a general proof was incorrect. Complete proofs were later presented by M. von Laue, C. Herring, and others. An anthology, with comments, of this early work (since Gibbs) is presented in the book by Schneer (1970).

Since the surface tensions depend upon the geometric distribution of the particles making up the crystal, the Wulff theorem establish a relation between the forms and the structure of crystals, and could be used for this study before the discovery of X-ray diffraction. Although it is not easy to find equilibrium crystals in nature one may think that an average of the ensemble of forms of a mineral species approach equilibrium.

It is only in recent times that equilibrium crystals have been produced in the laboratory. Most crystals grow under non-equilibrium conditions, as predicted by Gibbs, and is a subsequent relaxation of the macroscopic crystal that restores the equilibrium. This requires transport of material over long distances and the time scales can be very long, even for very small crystals. One has been able to study, however, metal crystals in equilibrium of size 1-10 micron. Equilibration times of a few days were observed. A schematic representation of a cubic equilibrium crystal is shown in Figure 1.

A very interesting phenomenon that can be observed on equilibrium crystals is the roughening transition. This transition is characterized by the disappearance of the facets of a given orientation from the equilibrium crystal, when the temperature attains a certain particular value. Roughening transitions have been found experimentally, first, in negative crystals (i.e., vapor bubbles included in a crystal) of organic substances. The best observations have been made on helium crystals in equilibrium with superfluid helium, since then the transport of matter and heat is extremely fast. Crystals grow to a size of 1-5 mm and relaxation times vary from milliseconds to minutes. Roughening transitions for three different types of facets have been observed (see, for instance, Wolf et al. 1983).

**Thermodynamics of equilibrium crystals**

The problem is to find, at equilibrium, the shape of a droplet of a phase \(c\), the crystal, inside a phase \(m\), called the medium.

Let \(\mathbf{n}\) be a unit vector in \(\mathbf{R}^d\) and consider the situation in which the phases \(c\) and \(m\) coexist over a plane perpendicular to \(\mathbf{n}\). Let \(\tau(\mathbf{n})\) be the surface
tension, or free energy per unit area, of such an interface. If $B$ is the set of $\mathbb{R}^d$ occupied by the phase $c$, and $\partial B$ the boundary of $B$, the total surface free energy of the crystal is given by

$$\tau(\partial B) = \int_{\xi \in \partial B} \tau(n(\xi)) ds_\xi$$

Here $n(\xi)$ is the exterior unit normal to $\partial B$ at $\xi$ and $ds_\xi$ is the element of area at this point. One has to minimize this expression under the constraint that the total (Lebesgue) volume $|B|$ occupied by the phase $c$ is fixed. Given a set $W$, we say that the crystal $B$ has shape $W$ if after a translation and a dilation it equals $W$.

The solution of this variational problem, known under the name of Wulff construction, is given by

$$W = \{x \in \mathbb{R}^d : x \cdot n \leq \tau(n) \text{ for every } n \in S^{d-1}\}$$

**Theorem 1** Let $W$ be the just defined Wulff shape for the surface tension function $\tau(n)$. Let $B \subset \mathbb{R}^d$ be any other region with sufficiently smooth boundary and the same (Lebesgue) volume as $W$. Then

$$\tau(\partial B) \geq \tau(\partial W)$$
with equality if and only if $B$ and $W$ have the same shape.

The proof presented here will be based, following Taylor (1987), on geometrical inequalities. First, one notices that being defined as the intersection of closed half-spaces, the Wulff shape $W$ is a closed, bounded convex set, i.e., a convex body. Among the functions $\tau(n)$, which through the above formula define the same shape $W$, there is a unique function having the property that all planes $\{x \in \mathbb{R}^d : x \cdot n = \tau(n)\}$, associated to all different unit vectors $n$, are tangent to the convex set $W$. This function is given by

$$\tau_W(n) = \sup_{x \in W} (x \cdot n)$$

and is called the support function of the convex body $W$. For an arbitrary function $\tau(n)$ defining the same Wulff shape $W$, it can be that some of these planes do not touch the set $W$. Thus, the function $\tau_W(n)$ is the smallest function on the unit sphere which gives the Wulff shape $W$.

Given the surface tension, consider its extension by positive homogeneity, $f(x) = |x| \tau(x/|x|)$. It turns out that if $f(x)$ is a convex function on $\mathbb{R}^d$, then $\tau(n)$ is the support function of the convex body $W$. This condition is also equivalent to the fact that the surface tension $\tau$ satisfies a thermodynamic stability condition called the pyramidal inequality, see Messager et al. (1992).

The following Theorem is an extension of the isoperimetric property.

**Theorem 2** Let $W \subset \mathbb{R}^d$ be a convex body and $\tau_W(n)$ the corresponding support function. For any set $B \subset \mathbb{R}^d$, with sufficiently smooth boundary, we have

$$\tau_W(\partial B) \geq d |W|^{1/d} |B|^{(d-1)/d}$$

where $|W|$, $|B|$, denote the (Lebesgue) volumes of $W$, $B$, respectively, and $\tau_W(\partial B)$ is the surface free energy of $\partial B$. The equality occurs only when $B$ and $W$ have the same shape.

If $D$ is the closed circle of unit radius with center at the origin, then the corresponding support function $\tau_D(n)$ is equal to the constant 1, and the Theorem reduces to the isoperimetric property: The area $F$ and the length $L$ of any plane domain satisfy the inequality $L^2 \geq 4\pi F$.

Theorem 2 is a consequence of the following Brunn-Minkowski inequality:

**Theorem 3** For non empty compact sets $A, B \subset \mathbb{R}^d$,

$$|A + B|^{1/d} \geq |A|^{1/d} + |B|^{1/d}$$
Moreover, the equality sign holds only when \( A \) and \( B \) are two convex bodies with the same shape (or one of the sets consists of a single point).

Given two non-empty sets \( A, B \subset \mathbb{R}^d \) their vector Minkowski sum is defined by \( A + B = \{ a + b : a \in A, b \in B \} \). A proof of Theorem 3 can be found in the book by Burago and Zalgaller (1988). First one proves by direct computation that the inequality holds in the case in which \( A \) and \( B \) are parallelepipeds with sides parallel to the coordinate axis. The validity of the inequality is then extended by induction to all finite unions of such parallelepipeds and, finally, to all compact sets by an appropriate limit process.

**Lemma** Let \( W \) be a convex body in \( \mathbb{R}^d \). Given any set \( B \subset \mathbb{R}^d \), with sufficiently smooth boundary, we can express the functional \( \tau_W(\partial B) \) as

\[
\tau_W(\partial B) = \lim_{\lambda \to 0} \frac{|B + \lambda W| - |B|}{\lambda}
\]

where \( \lambda W \) denotes the homothetic set \( \{ \lambda x : x \in W \} \). If \( B \subset \mathbb{R}^d \) is bounded, the functional \( \tau_W \) is well defined. In particular, this last formula shows that

\[
\tau_W(\partial W) = d |W|
\]

**Proof.** To prove this lemma, observe that if \( H(n) \) denotes the half space below a plane orthogonal to \( n \), and “dist” denotes the distance between two sets (two parallel planes), then, from the definition of \( \tau_W \),

\[
\tau_W(n) = \text{dist}(\partial H(n), \partial (H(n) + W))
\]

and one can then write

\[
\tau_W(\partial B) = \int_{\xi \in \partial B} \text{dist}(\partial H(n(\xi)), \partial (H(n(\xi)) + W))ds_\xi
\]

\[
= \int_{\xi \in \partial B} \lim_{\lambda \to 0} (1/\lambda)\text{dist}(\xi, \partial (B + \lambda W))ds_\xi
\]

This last expression coincides with the formula for \( \tau_W(\partial B) \) given in the Lemma, and proves its validity.

**Proof of Theorem 2.** The inequality in Theorem 2 then follows by applying the Brunn-Minkowski inequality to \( |B + \lambda W| \). This gives

\[
|B + \lambda W| - |B| \geq (|B|^{1/d} + \lambda |W|^{1/d})^d - |B| \geq d \lambda |B|^{(d-1)/d} |W|^{1/d}
\]

which, taking the Lemma into account, ends the proof of Theorem 2.
Proof of Theorem 1. Let $\mathcal{W}$ be the Wulff shape corresponding to the function $\tau$. Then

$$\tau(\partial B) \geq \tau_\mathcal{W}(\partial B) \geq d |\mathcal{W}|^{1/d}|B|^{(d-1)/d}$$

taking the remark into account, together with the isoperimetric inequality (Theorem 2). But, when $B = \mathcal{W}$, we have

$$\tau(\partial \mathcal{W}) = \tau_\mathcal{W}(\partial \mathcal{W}) = d |\mathcal{W}|$$

Here, the first equality follows from the fact that $\tau_\mathcal{W}(\mathbf{n}) \neq \tau(\mathbf{n})$ only for the unit vectors $\mathbf{n}$ for which the planes $\mathbf{x} \cdot \mathbf{n} = \tau(\mathbf{n})$ are not tangent to the convex set $\mathcal{W}$. The second equality follows from the remark. Therefore

$$\tau(\partial B) \geq \tau(\partial \mathcal{W}) (|B|/|\mathcal{W}|)^{(d-1)/d}$$

which, when $|B| = |\mathcal{W}|$, gives the inequality stated in Theorem 1. The equality in Theorem 1 corresponds to the equality in Theorem 2. This ends the proof of Theorem 1.

The appearance of a plane facet in the equilibrium crystal shape is related to the existence of a discontinuity in the derivative of the surface tension with respect to the orientation.

More precisely, let the surface tension $\tau(\mathbf{n}) = \tau(\theta, \phi)$, for $d = 3$, be expressed in terms of the spherical coordinates of $\mathbf{n}$, the vector $\mathbf{n}_0$ being taken as the $x_3$ axis, and assume that it satisfies the stability condition mentioned above. Then, $\tau(\mathbf{n})$ is the support function of the Wulff shape, and as a natural consequence of this fact (see Miracle-Sole 1995), it follows:

**Theorem 4** A facet orthogonal to $\mathbf{n}_0$ appears in the Wulff shape if, and only if, the derivative $\partial \tau(\theta, \phi)/\partial \theta$ is discontinuous at the point $\theta = 0$, for all $\phi$. The facet $\mathcal{F} \subset \partial \mathcal{W}$ consists of the points $\mathbf{x} \in \mathbb{R}^3$ belonging to the plane $x_3 = \tau(\mathbf{n}_0)$ and such that, for all $\phi$ between $0$ and $2\pi$,

$$x_1 \cos \phi + x_2 \sin \phi \leq \partial \tau(\theta, \phi)/\partial \theta \big|_{\theta=0}$$

**Proof.** In terms of the convex function $f(\mathbf{x}) = \tau(\mathbf{x}/|\mathbf{x}|)$, the Wulff shape $\mathcal{W}$ is the set of all $\mathbf{x} = (x_1, x_2, x_3) \in \mathbb{R}^3$ such that

$$x_1 y_1 + x_2 y_2 + x_3 y_3 \leq f(\mathbf{y})$$

for every $\mathbf{y} \in \mathbb{R}^3$. If the coordinate axes are placed in such a way that $\mathbf{n}_0 = (0, 0, 1)$, the plane $x_3 = \tau(0)$ (where $\tau(0)$ is the value of $\tau$ for $\theta = 0$) is
a tangent plane to \( W \). The facet \( F \) is the portion of this plane contained in \( W \). Accordingly, the facet \( F \) consists of the points \((x_1, x_2, \tau(0)) \in \mathbb{R}^3\) such that

\[
x_1y_1 + x_2y_2 \leq f(y_1, y_2, y_3) - y_3\tau(0) = f(y_1, y_2, y_3) - y_3f(0, 0, 1)
\]

for all \( y = (y_1, y_2, y_3) \). Or, equivalently, such that

\[
x_1y_1 + x_2y_2 \leq g(y_1, y_2) = \inf_{y_3} (f(y_1, y_2, y_3) - y_3f(0, 0, 1))
\]

Restricting the infimum to \( y_3 = 1/\lambda \geq 0 \), and using the positive homogeneity and the convexity of \( f \), one obtains

\[
g(y_1, y_2) = \lim_{\lambda \to 0, \lambda \geq 0} (1/\lambda) (f(\lambda y_1, \lambda y_2, 1) - f(0, 0, 1))
\]

This implies that \( g \) is a positively homogeneous convex function on \( \mathbb{R}^2 \). Define

\[
\mu(\phi) = g(\cos \phi, \sin \phi)
\]

Taking \( \lambda = \tan \theta \), one gets

\[
\mu(\phi) = \lim_{\theta \to 0, \theta \geq 0} (1/\sin \theta) (f(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) - \cos \theta f(0, 0, 1))
\]

\[
= \lim_{\theta \to 0, \theta \geq 0} (1/\theta) (\tau(\theta, \phi) - \tau(0)) = (\partial/\partial \theta)_{\theta=0^+} \tau(\theta, \phi)
\]

Similarly

\[
\mu(\phi + \pi) = g(- \cos \phi, - \sin \phi) = -(\partial/\partial \theta)_{\theta=0^-} \tau(\theta, \phi)
\]

Both one-sided derivatives of \( \tau \) exist and, from the convexity of \( g \), it follows that

\[
\mu(\phi + \pi) \leq \mu(\phi)
\]

Thus, the hypothesis of the discontinuity of the derivative \( \partial \tau/\partial \theta \), at \( \theta = 0 \), implies the strict inequality in the above equation, and shows that the convex set \( F \) has a non-empty interior.

### Interfaces in statistical mechanics

In a first approximation one can model the interatomic forces in a crystal by a lattice gas. In a typical two-phase equilibrium state there is, in these systems, a dense component, which can be identified as the crystal phase, and a
dilute component, which can be identified as the vapor phase. The underly-
ing lattice structure implies that the crystal phase is anisotropic, while this
assumption, though unrealistic for the vapor phase, should be immaterial for
the description of the crystal-vapor interface. As an illustrative example of
such systems, the ferromagnetic Ising model will be considered.

The Ising model is defined on the $d$-dimensional cubic lattice $\mathcal{L} = \mathbb{Z}^d$, with
configuration space $\Omega = \{-1, 1\}^\mathcal{L}$. The value $\sigma(i) = \pm 1$ is the spin at the
site $i \in \mathcal{L}$. The occupation numbers, $n(i) = (1/2)(\sigma(i) + 1) = 0$ or 1,
give the lattice gas version of this model. The energy of a configuration
$\sigma_\Lambda = \{\sigma(i), i \in \Lambda\}$, in a finite box $\Lambda \subset \mathcal{L}$, under the boundary conditions
$\bar{\sigma} \in \Omega$, is

$$H_\Lambda(\sigma_\Lambda | \bar{\sigma}) = -J \sum_{\langle i,j \rangle \cap \Lambda \neq \emptyset} \sigma(i)\sigma(j)$$

where $J > 0$, $\langle i,j \rangle$ are pairs of nearest neighbor sites, and $\sigma(i) = \bar{\sigma}(i)$ when
$i \notin \Lambda$. The partition function, at the inverse temperature $\beta = 1/kT$, is given
by

$$Z^\bar{\sigma}(\Lambda) = \sum_{\sigma_\Lambda} \exp \left( - \beta H_\Lambda(\sigma_\Lambda | \bar{\sigma}) \right)$$

This model presents, at low temperatures $T < T_c$, where $T_c$ is the critical
temperature, two distinct thermodynamic pure phases. This means two ex-
tremal translation invariant Gibbs states, which correspond to the limits,
when $\Lambda \to \infty$, of the finite volume Gibbs measures

$$Z^\bar{\sigma}(\Lambda)^{-1} \exp \left( - \beta H_\Lambda(\sigma_\Lambda | \bar{\sigma}) \right)$$

with boundary conditions $\bar{\sigma}$ respectively equal to the ground configurations
$(\,)$ and $(\,)$ (respectively, $\bar{\sigma}(i) = 1$ and $\bar{\sigma}(i) = -1$, for all $i \in \mathcal{L}$). Moreover,
they are the unique extremal translation invariant Gibbs states of the system
(Bodineau, 2006). On the other side, if $T \geq T_c$, the Gibbs state is unique.

Each configuration inside $\Lambda$ can be described in a geometric way by specifying
the set of Peierls contours which indicate the boundaries between the regions
of spin 1 and the regions of spin $-1$. Unit square faces are placed midway
between the pairs of nearest-neighbor sites $i$ and $j$, perpendicularly to these
bonds, whenever $\sigma(i)\sigma(j) = -1$. The connected components of this set of
faces are the Peierls contours. Under the boundary conditions $(\,)$ and $(\,)$,
the contours form a set of closed surfaces. They describe the defects of the
considered configuration with respect to the ground configurations, and are
a basic tool for the investigation of the model at low temperatures.
In order to study the interface between the two pure phases one needs to construct a state describing the coexistence of these phases. To simplify the exposition it will be assumed that $d = 3$. Let $\Lambda$ be a parallelepiped of sides $L_1, L_2, L_3$, parallel to the axes, and centered at the origin of $L$, and let $\mathbf{n} = (n_1, n_2, n_3)$ be a unit vector in $\mathbb{R}^3$, such that $n_3 \neq 0$. Introduce the mixed boundary conditions $(\pm, \mathbf{n})$, for which

$$\bar{\sigma}(i) = \begin{cases} 1 & \text{if } i \cdot \mathbf{n} \geq 0 \\ -1 & \text{if } i \cdot \mathbf{n} < 0 \end{cases}$$

These boundary conditions force the system to produce a defect going transversally through the box $\Lambda$, a big Peierls contour that can be interpreted as the microscopic interface. The other defects that appear above and below the interface can be described by closed contours inside the pure phases.

The free energy, per unit area, due to the presence of the interface, is the surface tension. It is defined by

$$\tau(\mathbf{n}) = \lim_{L_1, L_2 \to \infty} \lim_{L_3 \to \infty} -\frac{n_d}{\beta L_1 L_2} \ln \frac{Z(\pm, \mathbf{n})(\Lambda)}{Z(+)(\Lambda)}$$

In this expression the volume contributions proportional to the free energy of the coexisting phases, as well as the boundary effects, cancel, and only the contributions to the free energy due to the interface are left.

**Theorem 5** The thermodynamic limit $\tau(\mathbf{n})$, of the interfacial free energy per unit area, exists, and is a non negative bounded function of $\mathbf{n}$. Its extension by positive homogeneity, $f(\mathbf{x}) = |\mathbf{x}| \tau(\mathbf{x}/|\mathbf{x}|)$ is a convex function on $\mathbb{R}^3$.

A proof of these statements has been given by Messager et al. (1992) using correlation inequalities and, in fact, the Theorem holds for a large class of lattice systems. Moreover, for the Ising model we know, from Bricmont et al. (1980), Lebowitz and Pfister (1981), and the convexity condition, that $\tau(\mathbf{n})$ is strictly positive for $T < T_c$ and that it vanishes if $T \geq T_c$.

Consider now the microscopic interface orthogonal to the direction $\mathbf{n}_0 = (0, 0, 1)$. At low temperatures $T > 0$, we expect this interface, which at $T = 0$ coincides with the plane $i_3 = -1/2$, to be modified by deformations. It can be described by means of its defects, with respect to the interface at $T = 0$. These defects, called walls, form the boundaries between the smooth plane portions of the interface. In this way the interface structure may then be interpreted as a “gas of walls” on a two-dimensional lattice.
Dobrushin (1972) proved the dilute character of this gas at low temperatures, which means that the interface is essentially flat (or rigid). The considered boundary conditions yield indeed a non translation invariant Gibbs state. This is known also to be the case for all $T$ less than $T_{c}^{d=2}$, the critical temperature of the two-dimensional Ising model, from correlation inequalities (van Beijeren 1975). Notice that $J/kT_{c}^{d=2} = 0.44$ is the exact value, and that $J/kT_{c}^{d=3} \sim 0.22$ is the estimation in three dimensions. It will be seen, in the next Section, that the rigidity of the interface is related to the formation of a plane facet in the equilibrium crystal.

The same analysis applied to the two-dimensional model shows a different behavior at low temperatures. In this case Gallavotti (1972) proved that the microscopic interface undergoes large fluctuations and does not survive in the thermodynamic limit. The interface is rough and the corresponding Gibbs state is translation invariant.

Coming back to the three-dimensional Ising model, where the interface orthogonal to a lattice axis is known to be rigid at low temperatures, the following question arises: At higher temperatures, do the fluctuations of this interface become unbounded, in the thermodynamic limit, so that the corresponding Gibbs state is translation invariant?

One says then that the interface is rough. It is believed that, effectively, the interface becomes rough when the temperature is raised, undergoing a roughening transition at a temperature $T_{R}$ strictly smaller than the critical temperature $T_{c}$. Indeed, approximate methods give some evidence for the existence of such a $T_{R}$ and suggest a value near to $J/kT_{R} = 0.41$.

**Remark** It has been possible, over the last years, to justify the Wulff construction directly from a microscopic theory.

The first mathematically rigorous proof of the validity of the Wulff construction, in the case of the two-dimensional Ising model at low temperatures, is due to Dobrushin et al. (1992). See also Pfister (1991), for another version of the proof, and Miracle-Sole and Ruiz (1994) for a simpler approach in the case of an interface model.

These results show that, using the canonical ensemble, where the total number of particles (or the total magnetization in the language of spin systems) is fixed, if the configurations of the system are properly rescaled in the thermodynamic limit, then a (unique) droplet of the dense phase, immersed in the dilute phase, is formed. Its shape coincides with the Wulff shape. This
fact was later extended to all temperatures below the critical temperature. Recently, such a study has also been carried out in the case of three or more dimensions by Bodineau (1999), Cerf and Pitsztora (2000).

**Wulff shape in statistical mechanics**

Consider the surface tension in the Ising model, between the positive and negative phases, defined as in Theorem 5. In the two-dimensional case, this function $\tau(n)$ has (as shown by Abraham) an exact expression in terms of some Onsager’s function. It follows (as explained in Miracle-Sole 1999) that the Wulff shape $W$, in the plane $(x_1, x_2)$, is given by

$$\cosh \beta x_1 + \cosh \beta x_2 \leq \cosh^2 \frac{2\beta J}{\sinh 2\beta J}.$$

This shape reduces to the empty set for $\beta \leq \beta_c$, since the critical $\beta_c$ satisfies $\sinh 2J\beta_c = 1$. For $\beta > \beta_c$, it is a strictly convex set with smooth boundary.

In the three-dimensional case, only certain interface models can be exactly solved. Consider the Ising model at zero temperature, with boundary condition $(\pm, n)$. Then the ground configurations have only one defect, the microscopic interface $\lambda$, imposed by this condition, and

$$\tau(n) = \lim_{L_1, L_2 \to \infty} \frac{n_3}{L_1 L_2} (E_\Lambda(n) - \beta^{-1} N_\Lambda(n)),$$

where $E_\Lambda = 2J|\lambda|$ is the energy (all $\lambda$ have the same minimal area) and $N_\Lambda$ the number of the ground states. Every such $\lambda$ has the property of being cut only once by all straight lines orthogonal to the diagonal plane $i_1 + i_2 + i_3 = 0$, provided that $n_k > 0$, for $k = 1, 2, 3$. Each $\lambda$ can then be described by an integer function defined on a triangular plane lattice, the projection of the cubic lattice $L$ on the diagonal plane. The model defined by this set of admissible microscopic interfaces is precisely the TISOS model, introduced by Nienhuis et al. (1989). A similar definition can be given for the BCSOS model that describes the ground configurations on the body-centered cubic lattice (see van Beijeren 1977 and Kotecky, Miracle-Sole 1987).

From a macroscopic point of view, the roughness or the rigidity of an interface should be apparent when considering the shape of the equilibrium crystal associated with the system. A typical equilibrium crystal at low temperatures has smooth plane facets linked by rounded edges and corners. The area of a particular facet decreases as the temperature is raised and the facet finally
disappears at a temperature characteristic of its orientation. It can be argued that the disappearance of the facet corresponds to the roughening transition of the interface whose orientation is the same as that of the considered facet.

The exactly solvable interface models mentioned above, for which the function $\tau(n)$ has been exactly computed, are interesting examples of this behavior, and provide a valuable information on several aspects of the roughening transition. This subject has been reviewed in Kotecky (1989) and Miracle-Sole (1999). For example, Figure 1 shows the shape predicted by the TISOS model.

For the three-dimensional Ising model at positive temperatures, the description of the microscopic interface, for any orientation $n$, appears as a very difficult problem. It has been possible, however, to analyze the interfaces which are very near to the particular orientations $n_0$, discussed in the precedent Section. This analysis can be used to determine the shape of the facets in a rigorous way.

The step free energy plays a role in the facet formation, as shown in Theorems 6 and 7, below. It is defined as the free energy associated with the introduction of a step of height 1 on the interface, and can be regarded as an order parameter for the roughening transition. Let $\Lambda$ be, as in Section 2, a parallelepiped of sides $L_1, L_2, L_3$, parallel to the axes, centered at the origin, and introduce the (step, $m$) boundary conditions, associated to the unit vectors $m = (\cos \phi, \sin \phi) \in \mathbb{R}^2$, by

$$\bar{\sigma}(i) = \begin{cases} 
1 & \text{if } i_3 > 0 \text{ or if } i_3 = 0 \text{ and } i_1 m_1 + i_2 m_2 \geq 0, \\
-1 & \text{otherwise}.
\end{cases}$$

Then, the step free energy, per unit length, for a step orthogonal to $m$ (with $m_2 > 0$) on the horizontal interface, is

$$\tau_{\text{step}}(\phi) = \lim_{L_1 \to \infty} \lim_{L_2 \to \infty} \lim_{L_3 \to \infty} -\frac{\cos \phi}{\beta L_1} \ln \frac{Z_{\text{step},m}(\Lambda)}{Z^{z,n_0}(\Lambda)}.$$

A first result concerning the facet formation in the Wulff shape, was obtained by Bricmont et al. (1986), by proving a correlation inequality which establish $\tau_{\text{step}}(0)$ as a lower bound, strictly positif for $T < T^d_c$, to the one-sided derivative $\partial \tau(\theta, 0) / \partial \theta$ at $\theta = 0^+$ (the inequality extends to $\phi \neq 0$). Thus, when $\tau_{\text{step}} > 0$, a facet is expected, according to Theorem 4.

Using the perturbation theory of the horizontal interface, it is possible to study also the microscopic interfaces associated with the (step, $m$) boundary
conditions. When considering these configurations, the step may be viewed as an additional defect on the rigid interface described in Section 2. It is, in fact, a long wall going from one side to the other side of the box \( \Lambda \). The step structure at low temperatures can then be analyzed with the help of a new cluster expansion. As a consequence of this analysis we have the following theorem.

**Theorem 6** If the temperature is low enough, i.e., if \( \beta J \geq c_0 \), where \( c_0 \) is a suitable constant, then the step free energy, \( \tau_{\text{step}}(\phi) \), exists, is strictly positive, and extends by positive homogeneity to a strictly convex function. Moreover, \( \beta \tau_{\text{step}}(\phi) \) is an analytic function of \( \zeta = e^{-2J\beta} \), for which an explicit convergent series expansion can be found.

Using the above results on the step structure, similar methods allow us to evaluate the increment in surface tension of an interface tilted by a very small angle \( \theta \) with respect to the rigid horizontal interface. This increment can be expressed in terms of the step free energy and one obtains the following relation.

**Theorem 7** For \( \beta J \geq c_0 \), we have

\[
\frac{\partial \tau(\theta, \phi)}{\partial \theta} \bigg|_{\theta=0^+} = \tau_{\text{step}}(\phi).
\]

This relation, together with Theorem 4, implies that one obtains the shape of the facet by means of the two-dimensional Wulff construction applied to the step free energy. The reader will find a detailed discussion on these points, as well as the proofs of Theorems 6 and 7, in Miracle-Sole (1995).

From the properties of \( \tau_{\text{step}} \) stated in Theorem 6 it follows that the Wulff equilibrium crystal presents well defined boundary lines, smooth and without straight segments, between a rounded part of the crystal surface and the plane facets parallel to the three main lattice planes.

It is expected, but not proved, that at a higher temperature, but before reaching the critical temperature, the facets associated with the Ising model undergo a roughening transition. It is then natural to believe that the equality in Theorem 7 is true for any \( T \) lower than \( T_R \), and that for \( T \) higher than \( T_R \), both sides in this equality vanish, and thus, the disappearance of the facet is involved. However, the condition that the temperature is low enough is needed in the proofs of Theorems 6 and 7.
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