HAL
open science

Facet shapes in a Wulff crystal

Salvador Miracle-Sole

To cite this version:

Salvador Miracle-Sole. Facet shapes in a Wulff crystal. Mathematical Results in Statistical Mechanics, Satellite Colloquium of STATPHYS 20, 1998, Marseille, France. pp.83-101. hal-00706899

HAL Id: hal-00706899

https://hal.science/hal-00706899

Submitted on 11 Jun 2012

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Centre de Physique Théorique[1], CNRS Luminy, Case 907
F-13288 Marseille – Cedex 9

FACET SHAPES IN A WULFF CRYSTAL

Salvador MIRACLE-SOLE[2]

Abstract

According to the Wulff construction the shape of the equilibrium crystal is determined by the surface tension considered as a function of the interface orientation. We present some (conjectured) approximate solutions and some rigorous results concerning this function, in the case of a lattice gas, and apply them to study the shape of the equilibrium crystal and, in particular, the shape of the facets of this crystal.

Published in *Mathematical Results in Statistical Mechanics*, editors S. Miracle-Sole, J. Ruiz, V. Zagrebnov, World Scientific, Singapore, 1999 (ISBN 981-02-3863-0), pp. 83–101. Proceedings of the Satellite Colloquium of STAT-PHYS 20 held in Marseille, France, July 27–31, 1998.

Keywords: Surface tension; step free energy; equilibrium crystals; facets shape; Ising model; interface models.

Number of figures: 4

CPT-98/P. 3741

[1]Unité Propre de Recherche 7061
[2]Centre de Physique Théorique, CNRS, Marseille

1 Introduction

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 underlying 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 [1], [2]. 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 $\mathcal{L} = \mathbf{Z}^d$, 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

$$H_\Lambda(\sigma_\Lambda \mid \bar{\sigma}) = -J \sum_{\langle i,j \rangle \cap \Lambda \neq \emptyset} \sigma(i)\sigma(j) \tag{1}$$

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

$$Z^{\bar{\sigma}}(\Lambda) = \sum_{\sigma_\Lambda} \exp\big(- \beta H_\Lambda(\sigma_\Lambda \mid \bar{\sigma})\big) \tag{2}$$

The limit

$$f(\beta) = \lim_{\Lambda \to \infty} -\frac{1}{\beta |\Lambda|} \ln Z^{\bar{\sigma}}(\Lambda) \tag{3}$$

is independent of the boundary conditions and defines the free energy per unit volume.

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

$$Z^{\bar{\sigma}}(\Lambda)^{-1} \exp\big(- \beta H_\Lambda(\sigma_\Lambda \mid \bar{\sigma})\big) \tag{4}$$

with boundary conditions $\bar{\sigma}$ respectively equal to the ground configurations $(+)$ and $(-)$ (respectively, $\bar{\sigma}(i) = 1$ and $\bar{\sigma}(i) = -1$, for all $i \in \mathcal{L}$). On the other side, if $T \geq T_c$, the Gibbs state is unique.

Each configuration inside Λ 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 surfaces 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 are the Peierls contours. Under the boundary conditions $(+)$ and $(-)$, the contours form a set of closed surfaces. They can be viewed as defects, or excitations, with respect to the ground states of the system (the constant configurations 1 and -1), 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. Let Λ be a parallelepiped of sides L_1, L_2, L_3, parallel to the axes, and centered at the origin of $\mathcal{L}$, and let $\mathbf{n} = (n_1, n_2, n_3)$ be a unit vector in $\mathbf{R}^3$, such that $n_3 \neq 0$. Introduce the mixed boundary conditions $(\pm, \mathbf{n})$, for which

$$\bar{\sigma}(i) = \begin{cases} 1 & \text{if} \quad i \cdot \mathbf{n} \geq 0 \\ -1 & \text{if} \quad i \cdot \mathbf{n} < 0 \end{cases} \tag{5}$$

These boundary conditions force the system to produce a defect going transversally through the box Λ, 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

$$\tau(\mathbf{n}) = \lim_{L_1, L_2 \to \infty} \lim_{L_3 \to \infty} -\frac{n_d}{\beta L_1 L_2} \ln \frac{Z^{(\pm, \mathbf{n})}(\Lambda)}{Z^{(+)}(\Lambda)} \tag{6}$$

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 1. *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 $\mathbf{R}^3$.*

A proof of these statements has been given in ref. [3] using correlation inequalities (this being the reason for their validity for all β) and, in fact, the Theorem holds for a large class of lattice systems. The convexity of f is

equivalent to the fact that the surface tension τ satisfies a thermodynamic stability condition called the pyramidal inequality (see [3], [4]).

Moreover, for the Ising model we know, from Bricmont et al. [5], Lebowitz and Pfister [6], and the convexity condition, that $\tau(\mathbf{n})$ is strictly positive for $T < T_c$ and that it vanishes if $T \geq T_c$.

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. The solution to this problem, known under the name of Wulff construction, is the following set

$$\mathcal{W} = \{\mathbf{x} \in \mathbf{R}^3 : \mathbf{x} \cdot \mathbf{n} \leq \tau(\mathbf{n}) \text{ for every } \mathbf{n} \in \mathbf{S}^2\} \tag{7}$$

Notice that the problem is scale invariant, so that if we solve it for a given volume of the crystal phase, we get the solution for other volumes by an appropriate scaling. The set $\mathcal{W}$, which will be called the Wulff shape, gives the optimal shape for the crystal.

The Wulff construction can also be viewed as a geometric version of the Legendre transformation. Consider the function $f(\mathbf{x})$ defined in Theorem 1. From definition (7), we get

$$\mathcal{W} = \{\mathbf{x} \in \mathbf{R}^d : f^*(\mathbf{x}) \leq 0\} \tag{8}$$

where f^* is the Legendre transform

$$f^*(\mathbf{x}) = \sup_{\mathbf{y}} (\mathbf{x} \cdot \mathbf{y} - f(\mathbf{y})) \tag{9}$$

Actually $f^*(\mathbf{x}) = 0$, if $\mathbf{x} \in \mathcal{W}$, and $f^*(\mathbf{x}) = \infty$, otherwise.

We next introduce a function φ on $\mathbf{R}^2$ such that the graph of $x_3 = \varphi(x_1, x_2)$, for $x_3 > 0$, coincides with the boundary $\partial\mathcal{W}$ of the crystal shape. Since $\mathcal{W}$ is a convex body, symmetric with respect to the origin, φ is a concave function, and

$$\mathcal{W} = \{\mathbf{x} \in \mathbf{R}^3 : -\varphi(-x_1, -x_2) \leq x_3 \leq \varphi(x_1, x_2)\} \tag{10}$$

This means that $-\varphi$ is the Legendre transform of the projected surface tension $\tau_p = (1/n_3)\tau$, considered as a function on $\mathbf{R}^2$ of the slopes $u_1 = n_1/n_3, u_2 = n_2/n_3$. In other words,

$$\tau_p(u_1, u_2) = f(u_1, u_2, 1) \tag{11}$$

Indeed, from equations (8) and (9), we see that

$$-\varphi(u_1, u_2) = \sup_{u_1,u_2} (x_1 u_1 + x_2 u_2 - \tau_p(u_1, u_2)) \tag{12}$$

Formula (12) is known as the Andreev construction [7]). The interest of this approach comes from the fact that φ, and hence, the crystal shape itself, may be regarded as the free energy associated to a certain statistical mechanical Gibbs ensemble. We shall consider this ensemble in sections 2 and 3.

2 The two dimensional model

We next consider the Ising model on a square lattice, with two interaction parameters, J_1 in the horizontal direction and J_2 in the vertical direction. There is in this model an exact expression for the surface tension $\tau(\mathbf{n})$. However, we shall first discuss an approximate expression, which may represent this quantity in the low temperature region. It is obtained by restricting the sums in formula (6) to the ground configurations.

Let $\mathcal{G}^{\bar{\sigma}}(\Lambda)$ be the set of ground configurations in Λ under the boundary conditions $\bar{\sigma}$, and let $\mathcal{N}^{\bar{\sigma}}(\Lambda)$ and $E_0^{\bar{\sigma}}(\Lambda) = H_\Lambda(\sigma|(\pm, \mathbf{n})) - H_\Lambda(+|(+))$ be the number and the relative energy of such configurations. The set $\mathcal{G}^+(\Lambda)$ contains only the configuration $(+)$ and, therefore,

$$\begin{aligned}\tau(\mathbf{n}) &= \lim_{L_1\to\infty} \lim_{L_2\to\infty} -\frac{n_2}{\beta L_1} \ln \sum_{\sigma\in\mathcal{G}^{(\pm,\mathbf{n})}(\Lambda)} e^{-\beta H_\Lambda(\sigma|(\pm,\mathbf{n}))+\beta H_\Lambda(+|(+))} \\ &= \lim_{L_1\to\infty} \lim_{L_2\to\infty} -\frac{n_2}{L_1}(E_0^{(\pm,\mathbf{n})}(\Lambda) - \beta^{-1} \ln \mathcal{N}^{(\pm,\mathbf{n})}(\Lambda))\end{aligned} \tag{13}$$

Notice that, in dimension two, if $\mathbf{n} = (-\sin\theta, \cos\theta)$ and $\tau(\theta) = \tau(\mathbf{n})$, then $v = -\tan\theta$ and the projected surface tension is $\tau_p(v) = \tau(\theta)/\cos\theta$. The configurations in $\mathcal{G}^{(\pm,\mathbf{n})}(\Lambda)$ contain only one Peierls contour, the microscopic interface, a polygonal line joining two fixed points in the boundary of Λ. This line is cut only once by all straight lines parallel to the diagonal $i_1 - i_2 = 0$. It can then be described by N integers

$$\phi(0), \phi(1), \ldots, \phi(N) \tag{14}$$

such that

$$n(i) = \phi(i) - \phi(i-1) = \pm 1, \quad i = 1, \ldots, N \tag{15}$$

specifying the heights, in units $1/\sqrt{2}$, over the line $i_1 + i_2 = 0$, of the extremities of the N consecutive unit segments which compose the polygonal line (see Figure 1). Writing $u = \tan(\pi/2 + \theta)$, the boundary conditions are

$$\phi(0) = 0, \quad \phi(0) - \phi(N) = uN \tag{16}$$

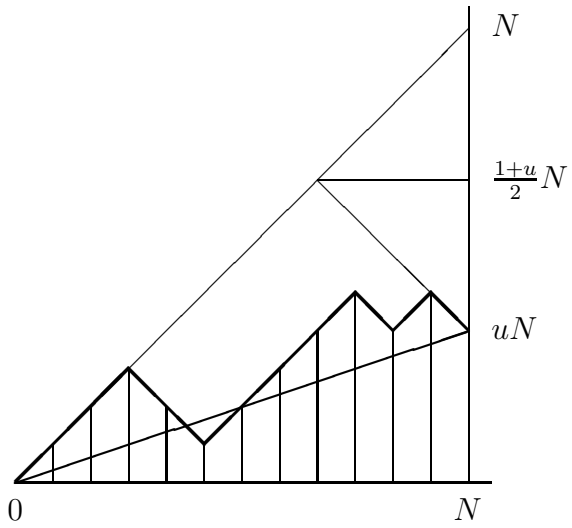

Figure 1. Description of a ground microscopic interface in 2 dimensions.

Under these boundary conditions we have that $n(i) = 1$, $\frac{1+u}{2}N$ times, and $n(i) = -1$, $\frac{1-u}{2}N$ times. All these configurations have the same energy

$$E^u(N) = 2J_1\frac{1+u}{2}N + 2J_1\frac{1-u}{2}N \tag{17}$$

and their number is

$$\mathcal{N}^u(N) = \binom{N}{\frac{1+u}{2}N} \tag{18}$$

Therefore, from equation (13), we get

$$\begin{aligned}\tau_p(u) &= J_1(1+u) + J_2(1-u) - \lim_{N\to\infty}\frac{1}{\beta N}\ln\frac{N!}{(\frac{1+u}{2}N)!(\frac{1-u}{2}N)!} \\ &= J_1(1+u) + J_2(1-u) + \frac{1}{\beta}\Big(\frac{1+u}{2}\ln\frac{1+u}{2} + \frac{1-u}{2}\ln\frac{1-u}{2}\Big)\end{aligned} \tag{19}$$

In order to obtain the equilibrium crystal shape we use the Andreev construction (12). In dimension two, we have

$$-\varphi(\xi) = \sup_u (\xi u - \tau_p(u)) \tag{20}$$

From u_0, solution of

$$\xi = \frac{d\tau_p}{du} = J_1 - J_2 + \frac{1}{2\beta} \ln \tfrac{1+u}{1-u} \tag{21}$$

that is

$$\tfrac{1+u_0}{1-u_0} = e^{2\beta\xi + 2\beta J_1 - 2\beta J_2} \tag{22}$$

$$u_0 = \frac{e^{2\beta\xi + 2\beta J_1 - 2\beta J_2} - 1}{e^{2\beta\xi + 2\beta J_1 - 2\beta J_2} + 1} \tag{23}$$

we find

$$\begin{aligned}
\varphi(\xi) &= -\xi u_0 + \tau_p(u_0) \\
&= -\xi u_0 + J_1 + J_2 + u_0(J_1 - J_2) + \frac{1}{2\beta}\Big(\ln \tfrac{1+u_0}{1-u_0} + 2 \ln \frac{1-u_0}{2} + u_0 \ln \tfrac{1+u_0}{1-u_0} \Big) \\
&= -\xi u_0 + J_1 + J_2 + u_0(J_1 - J_2) + (1+u_0)(\xi + J_1 - J_2) + \frac{1}{\beta} \ln \frac{1-u_0}{2} \\
&= \xi + 2J_1 - \frac{1}{\beta} \ln \left(1 + e^{2\beta\xi + 2\beta J_1 - 2\beta J_2}\right)
\end{aligned} \tag{24}$$

Next, we define the partition function

$$\Xi_N(\xi) = \sum_\phi e^{-\beta H(\phi) + \beta\xi(\phi(N) - \phi(0))} \tag{25}$$

where the sum runs over all configurations with $\phi(0) = 0$. We can interpret (25) as a "grand canonical" partition function with respect to the interface boundaries, and the restriction (16) in (13) as a "canonical" constraint. Since

$$\phi(N) - \phi(0) = \sum_{i=1}^N n(i) \tag{26}$$

$$H(\phi) = 2J_1 \delta(n(i) - 1) + 2J_2 \delta(n(i) + 1) \tag{27}$$

we have

$$\Xi_N(\xi) = \left(e^{-\beta(2J_1 - \xi)} + e^{-\beta(2J_2 + \xi)}\right)^N \tag{28}$$

and the corresponding free energy is

$$\varphi(\xi) = \lim_{N\to\infty} -\frac{1}{\beta N} \ln \Xi_N(\xi) \tag{29}$$

$$= -\frac{1}{\beta} \ln \left(e^{-\beta(2J_1-\xi)} + e^{-\beta(2J_2+\xi)}\right) \tag{30}$$

$$= \xi + 2J_1 - \frac{1}{\beta} \ln \left(1 + e^{2\beta\xi+2\beta J_1-2\beta J_2}\right) \tag{31}$$

Expressions (31) and (25) coincide. This means that φ, the free energy defined by (29), is the Legendre transform of τ_p, in agreement with the equivalence of the corresponding "canonical" and "grand canonical" ensembles. This fact illustrates the remark at the end of the introduction.

Putting $\eta = \eta(\xi) = \varphi(\xi)$, equation (31) can be written

$$e^{\beta(\eta-\xi-2J_1)} + e^{\beta(\eta+\xi-2J_2)} = 1 \tag{32}$$

for $\eta > 0$. Then, by using the initial coordinates $x = \eta + \xi$, $y = \eta - \xi$, and the symmetries of the figure, we obtain the following expression for the Wulff shape

$$\exp(\beta|x| - 2K_1) + \exp(\beta|y| - 2K_2) \leq 1 \tag{33}$$

Here $K_i = \beta J_i$, for $i = 1, 2$. This is the approximate solution. We next describe the exact solution.

It has been shown that

$$y = y(x) = \sup_v (xv - \tau_p(v)) \tag{34}$$

is, up to a factor, the Onsager function $\hat{\gamma}(\omega)$ for an imaginary argument, namely, $y(x) = \beta^{-1}\hat{\gamma}(-i\beta x)$. This means that

$$\cosh \beta y = \cosh 2K_1 \cosh 2K_2^* - \sinh 2K_1 \sinh 2K_2^* \cosh \beta x \tag{35}$$

where

$$K_i^* = -(1/2) \ln \tanh K_i \tag{36}$$

is the dual interaction constant ($i = 1, 2$). This is a result due to Abraham (see [8]). Taking into account that relation (36) implies $\cosh 2K_i^* \tanh 2K_i = 1$ and $\sinh 2K_i^* \sinh 2K_i = 1$, we get

$$\frac{\tanh 2K_2}{\cosh 2K_1} \cosh \beta x + \frac{\tanh 2K_1}{\cosh 2K_2} \cosh \beta y \leq 1 \tag{37}$$

as the exact expression for the Wulff shape. This simple expression has not appear in the literature, as far as we know. Several authors (see, for instance, [9]) have used the more complicated formula for the surface tension $\tau(\mathbf{n})$, which includes implicit functions, instead of the function $y(x)$.

The critical inverse temperature β_c satisfies $K_1 = K_2^*$ or $K_2 = K_1^*$ or, equivalently,

$$\sinh 2K_1 \sinh 2K_2 = 1 \tag{38}$$

In the symmetric case, $K_1 = K_2 = K$, we have $\sinh 2K_c = 1$ and $K_c = (1/2)\ln(\sqrt{2}+1) = 0.440687$. Now, notice that the left hand side of (37) is

$$\geq \frac{\tanh 2K_2}{\cosh 2K_1} + \frac{\tanh 2K_1}{\cosh 2K_2} = \frac{\sinh 2K_2 + \sinh 2K_1}{\cosh 2K_1 \cosh 2K_2} \tag{39}$$

The value of expression (39) equals 1 for $\beta = \beta_c$, because

$$\begin{aligned}(\sinh 2K_2 + \sinh 2K_1)^2 &= 2 + \sinh^2 2K_1 + \sinh^2 2K_1 \\ &= (1+\sinh^2 2K_1)(1+\sinh^2 2K_1) = \cosh^2 2K_1 \cosh^2 2K_2\end{aligned} \tag{40}$$

This implies that the Wulff shape reduces to the empty set for $\beta \leq \beta_c$. It has a finite positive volume for $\beta \geq \beta_c$.

A comparison of expressions (32) and (37) shows that the error made when considering the approximate solution (32) decreases exponentially in β when $\beta \to \infty$. However, the shape given by (32) presents four corners (when the boundary cuts the axes), while that corresponding to (37) has a smooth boundary. The same bound on the error can be proven by means of a low temperature cluster expansion for the function y, independently of the exact solution. This error is less than 1 % for temperatures less than $(1/2)T_c$. In the symmetric case the shape defined by (32) becomes the empty set at $K_c' = (1/2)\ln 2 = 0.346574$. We have $K_c' < K_c$.

3 The three dimensional model: Approximate solution

In this section we consider the Ising model on a cubic lattice and study the problem of finding in this case an approximate solution for the equilibrium crystal shape, analogous to that of section 2. The system so obtained is very interesting in itself, though its validity as a low temperature approximation is not known.

The ground configurations in $\mathcal{G}^{(\pm,\mathbf{n})}(\Lambda)$ contain only one Peierls contour, the microscopic interface. This contour is a surface made of unit squares such that its boundary is a fixed line determined by the boundary conditions $(\pm,\mathbf{n})$ on the faces of the box Λ. This contour has also the property of being cut only once by all straight lines orthogonal to the diagonal plane $i_1+i_2+i_3=0$. It can therefore be described by specifying the distance, or height, of each vertex of the unit squares, which form the contour, to the plane $i_1+i_2+i_3=0$. Now, the projection of the cubic lattice $\mathbf{Z}^3$ onto the plane $i_1+i_2+i_3=0$ is a triangular plane lattice, which will be denoted by $\mathcal{T}$. This means that, to each point $t\in\mathcal{T}$, we associate an integer variable $\phi(t)$ which, multiplied by the factor $1/\sqrt{3}$, gives the height of the microscopic interface at this point. The height differences

$$n(t,t')=\phi(t)-\phi(t') \tag{41}$$

between nearest neighbors t and t' obtained in this way are subject to the following restriction: Going clockwise along the edges of each elementary triangle pointing to the right the values of $n(t,t')$ are $\{1,1,-2\}$. An equivalent condition is obtained by using the triangles pointing to the left and to follow a counterclockwise path (see Figure 2). Conversely, from each configuration $\phi(t)$, $t\in\mathcal{T}$, subject to these restrictions, one can obtain a configuration of the microscopic interface. and, hence, a ground configuration in $\mathcal{G}^{(\pm,\mathbf{n})}(\Lambda)$,

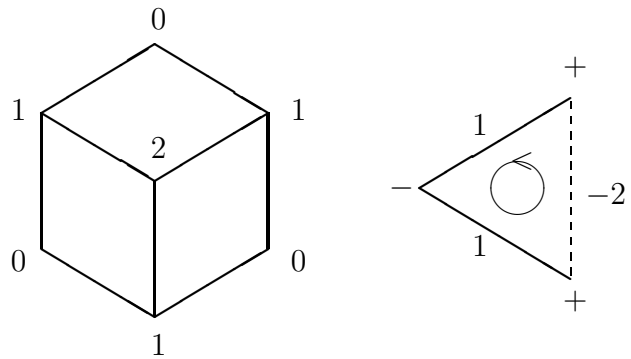

Figure 2. (a) Projection of a cube and heights of the vertices. (b) TISOS height differences as obtained from a ground configuration of the triangular Ising antiferromagnet. The corresponding diamond configuration is obtained by erasing the edges connecting parallel spins.

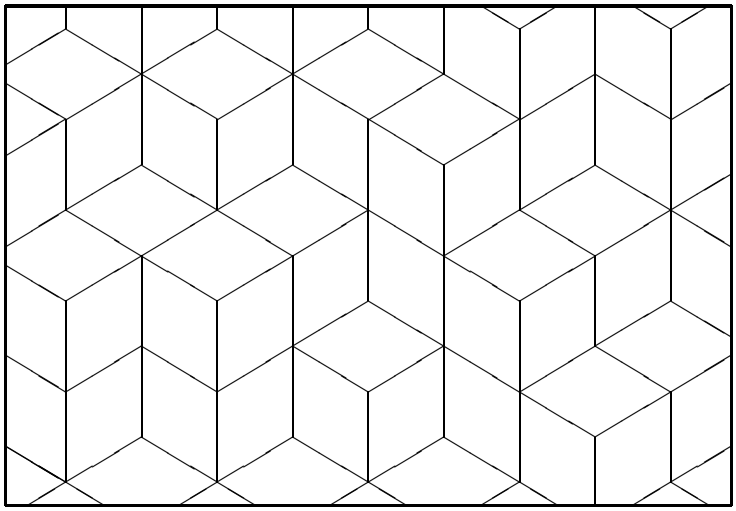

Figure 3. Illustration of the mapping of a ground microscopic interface in 3 dimensions onto a diamond configuration. A diamond configuration is obtained by erasing one edge in every elementary triangle of the triangular lattice.

provided that the boundary conditions are satisfied. The model with such a set of configurations was introduced in ref. [11] and considered also in ref. [12]. It is called the TISOS (triangular Ising solid-on-solid) model.

There is a one-to-one correspondence between the TISOS configurations and the allowed configurations of the Ising antiferromagnet at zero temperature. One can obtain it by requiring that odd and even height variables correspond to spins of different sign. It is easily checked that this Ising configuration obeys the $T = 0$ antiferromagnetic constraint that no elementary triangle should contain three spins with equal signs.

If one erases all lattice edges between parallel spins, one obtains a plane filled with rhombi or diamonds, as shown in Figure 3. Such a diamond covering is just the orthogonal projection on the diagonal plane of the edges of the microscopic interface initially considered on the cubic lattice. It gives also a view in perspective of this interface in the three dimensional space.

Let $\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{e}_3$ be three vectors on the plane at angles $2\pi/3$ and modulus equal to $\sqrt{3}/2$. Since the length of the edges of $\mathcal{T}$ is $\sqrt{3}/2$, the sites of the lattice $\mathcal{T}$ are of the form $t_1\mathbf{e}_1 + t_2\mathbf{e}_2$, with integer coordinates t_1, t_2. Let Q be the set of lattice sites inside the parallelogram defined by $|t_1| \leq L_1$ and $|t_2| \leq L_2$. Let $|Q|$ be the area of this parallelogram and let ∂Q be the boundary of Q (i.e., the set of sites in Q having some neighbor outside Q).

The boundary conditions corresponding to the slope $u = (u_1, u_2)$ are

$$\phi(t) = \bar{\phi}_u(t) = [u_1 i_1 + u_2 i_2], \quad i \in \partial Q \tag{42}$$

where $[\cdot]$ denotes the integer part. The corresponding projected surface tension is given by

$$\tau_p(u_1, u_2) = \lim_{L_1, L_2 \to \infty} -\frac{1}{\beta |Q|} Z_\Lambda(u_1, u_2) \tag{43}$$

with

$$Z_\Lambda(u_1, u_2) = \sum e^{-\beta H(\phi)} \tag{44}$$

In (44) the sum runs over all configurations ϕ inside Q satisfying the boundary conditions (42), and $H(\phi) = H_\Lambda(\sigma_\phi|(\pm, \mathbf{n})) - H_\Lambda(+|(+))$ is the relative energy of the ground configuration σ_ϕ associated to the microscopic interface defined by ϕ.

We can interpret the conditions (42) as "canonical" constraints and introduce a conjugate Gibbs ensemble of (44), which can be viewed as a "grand

canonical" ensemble with respect to the interface boundaries. For this purpose we consider the boundary terms

$$S_1(\phi) = \sum_{\ell \in \ell_1(Q)} n(\ell) \ , \quad S_2(\phi) = \sum_{\ell \in \ell_2(Q)} n(\ell) \tag{45}$$

where $\ell_1(Q)$ and $\ell_2(Q)$ are the sets of all bonds in Q parallel to the vectors $\mathbf{e}_1$ and $\mathbf{e}_2$, respectively, and oriented according to increasing coordinates. The bond variables $n(\ell)$ are the height differences of formula (41). The grand canonical prescription, which is convenient to consider, consists in adding to the energy a term of the form

$$x_1 S_1(\phi) + x_2 S_2(\phi) \tag{46}$$

where $x = (x_1, x_2) \in \mathbf{R}^2$ represent the slope "chemical" potentials. The associated partition function and free energy are

$$\Xi_Q^{\mathrm{per}}(x_1, x_2) = \sum_{\phi} e^{-\beta H(\phi) + \beta x_1 S_1(\phi) + \beta x_2 S_2(\phi)} \tag{47}$$

$$\varphi_Q^{\mathrm{per}}(x_1, x_2) = -\frac{1}{\beta |Q|} \ln \Xi_Q^{\mathrm{per}}(x_1, x_2) \tag{48}$$

The sum in (47) runs over all configurations in Q with periodic boundary conditions (with respect to the bond variables $n(\ell)$), $\phi(0)$ is taken equal to 0.

Theorem 2. *The limit, when $Q \to \infty$, of φ_Q^{per}, exists and equals*

$$\varphi(x_1, x_2) = -\sup_u \{x_1 u_1 + x_2 u_2 - \tau_p(u_1, u_2)\} \tag{49}$$

in the interior of the domain of the concave function φ.

The theorem is proved in ref. [10] for many SOS models. Notice that the partition function (48) does not correspond exactly to the conjugate ensemble of the function (44), as conditions (42) represent many more constraints that just fixing the values of the two sums in (45). The domain of a concave function $\varphi(x)$ is the set $\{x \in \mathbf{R}^2 : \varphi(x) > -\infty\}$.

It turns out that the free energy function $\varphi(x)$ of the TISOS model can be computed exactly. There is no additional difficulty in considering, like in section 1, an asymmetric Ising model on the cubic lattice (with three different interaction parameters in the vertical and the two horizontal directions).

However, it is interesting instead to introduce a new kind of asymmetry, and to take the interaction parameters equal to J_1, J_2 or J_3, according to whether the coordinates of the highest point of the corresponding bond satisfy $i_1 + i_2 + i_3 \equiv 0, 1,$ or 2 (mod 3).

Then, with $K_i = \beta J_i$ for $i = 1, 2, 3$, we write

$$\begin{aligned} r_1 &= \exp(-K_1 + K_2 + K_3) \\ r_2 &= \exp(K_1 - K_2 + K_3) \\ r_3 &= \exp(K_1 + K_2 - K_3) \\ r_0^3 &= r_1 r_2 r_3 \;=\; \exp(K_1 + K_2 + K_3) \end{aligned} \tag{50}$$

and

$$R = (r_1^3 + r_2^3 + r_3^3) r_0^{-3} \tag{51}$$

For reasons of symmetry, the grand canonical prescription, which will be considered, consists in adding to the energy, instead of the term (46), a term of the form

$$x_1 S_1(\phi) + x_2 S_2(\phi) + x_3 S_3(\phi), \quad \text{with } S_3(\phi) = \sum_{\ell \in \ell_3(Q)} n(\ell) \tag{52}$$

where $x_3 \in \mathbf{R}$ and $\ell_3(Q)$ is the set of all bonds in Q parallel to the vector $\mathbf{e}_3$. Taking, $X_i = \beta x_i$, for $i = 1, 2, 3$, we write

$$\begin{aligned} w_1 &= \exp(-X_1 + X_2 + X_3) \\ w_2 &= \exp(X_1 - X_2 + X_3) \\ w_3 &= \exp(X_1 + X_2 - X_3) \\ w_0^3 &= w_1 w_2 w_3 \;=\; \exp(X_1 + X_2 + X_3) \end{aligned} \tag{53}$$

Then, we have

$$\begin{aligned} \varphi \;&=\; \lim_{L_1, L_2 \to \infty} \frac{2}{L_1 L_2} \ln \Xi \;=\; \ln(w_0/r_0) + \\ &\frac{1}{24\pi^2} \int_0^{2\pi} dp \int_0^{2\pi} dq \, \ln \left| R w_0^3 e^{ip} + w_1^3 e^{3ip} - w_2^3 e^{-3iq} + w_3^3 e^{3iq} \right|^2 \end{aligned} \tag{54}$$

The exact solution (54) for the free energy of the model is due to Nienhuis et al. [12] (where slightly different notations are used). A careful study of

this solution, also in ref. [12], shows the existence of four regions in which the function φ has simple expressions, as indicated below

1) if $-w_1^3 + w_2^3 + w_3^3 + R\, w_0^3 \leq 0, \quad \varphi = \ln w_1 + \ln (w_0/r_0)$

2) if $w_1^2 - w_2^3 + w_3^3 + R\, w_0^3 \leq 0, \quad \varphi = \ln w_2 + \ln (w_0/r_0)$

3) if $w_1^3 + w_2^3 - w_3^3 + R\, w_0^3 \leq 0, \quad \varphi = \ln w_3 + \ln (w_0/r_0)$

4) if $w_1^3 + w_2^3 + w_3^3 - R\, w_0^3 \leq 0, \quad \varphi = \varphi_0$

In regions 1), 2) and 3), φ is a linear function of the variables x_1, x_2, x_3. It is constant in region 4), where it takes the value of (54) at the point $x_1 = x_2 = x_3 = 0$. These regions correspond to the domains of four ordered phases of the TISOS model in the phase diagram of this system.

According to the Andreev construction, the graph of the function

$$z = -(1/\beta)\, \varphi(x_1, x_2) \tag{55}$$

gives the boundary of the Wulff shape for the equilibrium crystal (equation (10)). The factor $-1/\beta$ comes from definition (54) in order to obtain the correct free energy. We have, in region 3), for instance,

$$z = J_1 + J_2 + J_3 - 2(x_1 + x_2) \tag{56}$$

which shows that the Wulff shape contains a plane facet orthogonal to the (0,0,1) direction. The boundary of this facet is determined by the boundary of region 3). The other regions 1), 2) and 4) indicate the existence of three other facets respectively orthogonal to the (1,0,0), (0,1,0) and (1,1,1) directions. The portion outside these regions corresponds to the curved part of the crystal surface.

It is only in recent times that equilibrium crystals have been produced in the laboratory, information and references on this subject can be found in the review articles [1] and [2]. As in the present model, 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, a phenomenon known under the name of roughening transition. The reader will find in ref. [12] a study of the roughening transition for the

(1,1,1) facet in the TISOS model, as well as a discussion on several other interesting properties of the crystal shape.

In the symmetric case, in which the interaction parameters of the Ising model are equal, $J_1 = J_2 = J_3 = J$, we have $R = 3$ (from equations (50) and (51)). Then the region of phase 4) is empty and the (1,1,1) facet does not exist. This follows from the algebraic identity

$$\begin{aligned} &w_1^3 + w_2^3 + w_3^3 - 3w_1w_2w_3 = \\ &(w_1 + w_2 + w_3)(w_1^2 + w_2^2 + w_3^2 - w_1w_2 - w_2w_3 - w_3w_1) = \\ &\tfrac{1}{2}(w_1 + w_2 + w_3)((w_1 - w_2)^2 + (w_2 - w_3)^2 + (w_3 - w_1)^2) \end{aligned} \tag{57}$$

showing that

$$w_1^3 + w_2^3 + w_3^3 - 3w_0^3 \geq 0 \tag{58}$$

Conversely, in the case that J_1, J_2 and J_3 are not equal one has $R > 3$ and expression (58) can be negative. Then region 4) is not empty if β is large enough, which implies the appearance of the (1,1,1) facet at low temperatures.

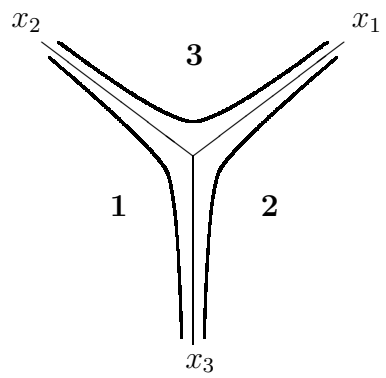

Figure 4. Equilibrium crystal shape according to the TISOS model in the symmetric case. The crystal is shown in a projection parallel to the (1,1,1) direction. The three regions 1), 2) and 3) indicate the facets, and the remaining area represents the curved part of the crystal surface.

Figure 4 shows a (1,1,1) corner of the crystal for the symmetric case $J_1 = J_2 = J_3 = J$. In this case the definition of region 3), for instance, can be written, using again identity (57),

$$\begin{aligned} &w_1^3 + w_2^3 - w_3^3 + 3w_1w_2w_3 = \\ &\tfrac{1}{2}(w_1 + w_2 - w_3)((w_1 - w_2)^2 + (w_2 + w_3)^2 + (-w_3 - w_1)^2) \leq 0 \end{aligned} \tag{59}$$

or, equivalently,

$$w_1 + w_2 - w_3 \leq 0 \tag{60}$$

and, using (53) with $x_3 = 0$, we see that region 3) can be defined by

$$e^{-2\beta x_1} + e^{-2\beta x_2} \leq 1 \tag{61}$$

The comparison of this formula with equation (33) shows the following statement.

Remark. The shape of the facets of the equilibrium crystal associated with the TISOS model, in the symmetric case, coincide with the Wulff shape obtained from the approximate solution of the two dimensional Ising model.

This property can be derived, without using the exact solution (54), with the help of the results of section 4 below, in particular Corollary 1. These results apply also to the TISOS model, and the shape of the facet is obtained by computing the corresponding $\tau^{\text{step}}(\mathbf{m})$. Notice also that the model can be used to describe the (1,1,1) corner of the crystal, that is 1/8 of the crystal. Completing it by symmetry we see that its facets undergo a roughening transition at $K_c' = (1/2)\ln 2 = 0.346574$ (see last paragraph of section 2), and we have $K_c' > K_c(3)$, where $K_c(3) \sim 0.22$ is the value of the critical coupling constant for the three dimensional Ising model.

There are other models for which an analysis similar to that of the present section could be developed. For example, the Ising model on a body centered cubic lattice with nearest and next nearest neighbor interactions is one of these models. This system leads also to an approximate solution that can be expressed in terms of exactly solvable SOS models (see [13] and the references quoted there).

4 The three dimensional model: Rigorous results

In the previous section we have described the microscopic interfaces at zero temperature for the Ising model on a cubic lattice. Some properties of these interfaces were studied by means of the exact solution of an associated SOS model. At low (positive) temperature we expect the ground interfaces to be modified by deformations. Small deformations will appear here and there, the large deformations having a very small probability. It appears, however, very difficult to develop such an argument into a rigorous proof that could justify the validity at low temperatures of the approximate solution described in section 3.

The situation is different for the interface orthogonal to the direction $\mathbf{n}_0 = (0, 0, 1)$. In this case there is, at zero temperature, only one microscopic interface, which coincides with the horizontal plane. The small deformations of this interface that appear at low temperatures are accessible to a mathematical treatment. The interface is rigid at low temperatures and its properties can be studied by means of a convergent cluster expansion. By pursuing this analysis it has been possible to determine the shape of the facets in a rigorous way. It can then be seen [14], from the proof of Theorem 3 below and Corollary 1, that this shape differs from the Wulff shape associated with the two dimensional Ising model, only by a quantity of order $\exp(-12\beta J)$, and thus, that it is close to the shape predicted by the approximate solution of section 3.

The appearance of a facet in the equilibrium crystal shape is related, according to the Wulff construction, to the existence of a discontinuity in the derivative of the surface tension with respect to the orientation. More precisely, assume that the surface tension satisfies the convexity condition of Theorem 1, and let this function $\tau(\mathbf{n}) = \tau(\theta, \phi)$ be expressed in terms of the spherical co-ordinates $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$ of $\mathbf{n}$, the vector $\mathbf{n}_0$ being taken as the x_3 axis. A facet orthogonal to the direction $\mathbf{n}_0$ appears in the Wulff shape $\mathcal{W}$ if, and only if, the derivative $\partial\tau(\theta, \phi)/\partial\theta$ is discontinuous at the point $\theta = 0$, for all ϕ. Moreover, the one-sided derivatives with respect to θ exist, at $\theta = 0^+$ and $\theta = 0^-$, and determine the shape of the facet. The facet $\mathcal{F} \subset \partial\mathcal{W}$ consists of the points $\mathbf{x} \in \mathbf{R}^3$ belonging to the plane $x_3 = \tau(\mathbf{n}_0)$ and such that

$$x_1 \cos\phi + x_2 \sin\phi \leq \partial\tau(\theta, \phi)/\partial\theta \,|_{\,\theta=0^+} \tag{62}$$

for every ϕ between 0 and 2π. A proof of this fact can be found in ref. [14] (Theorem 1).

The step free energy is expected to play an important role in the facet formation. It is defined as the free energy (per unit length) 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 Λ be a parallelepiped of sides L_1, L_2, L_3, parallel to the axes, and centered at the origin, and introduce the $(\text{step}, \mathbf{m})$ boundary conditions, associated to the unit vectors $\mathbf{m} = (\cos\phi, \sin\phi) \in \mathbf{R}^2$, by

$$\bar{\sigma}(i) = \begin{cases} 1 & \text{if } \ i > 0 \ \text{ or if } \ i_3 = 0 \ \text{ and } \ i_1 m_1 + i_2 m_2 \geq 0 \\ -1 & \text{otherwise} \end{cases} \tag{63}$$

Then, the step free energy, for a step orthogonal to $\mathbf{m}$ (with $m_2 \neq 0$) on the interface orthogonal to $\mathbf{n}_0 = (0, 0, 1)$, is

$$\tau^{\text{step}}(\phi) = \lim_{L_1\to\infty} \lim_{L_2\to\infty} \lim_{L_3\to\infty} -\frac{\cos\phi}{\beta L_1} \ \ln \ \frac{Z^{(\text{step},\mathbf{m})}(\Lambda)}{Z^{(\pm,\mathbf{n}_0)}(\Lambda)} \tag{64}$$

A first result concerning this point, was obtained by Bricmont et al. [15]. These authors proved a correlation inequality which establish $\tau^{\text{step}}(0)$ as a lower bound to the one-sided derivative $\partial\tau(\theta, 0)/\partial\theta$ at $\theta = 0^+$ (the inequality extends also to $\phi \neq 0$, see [14]). Thus when $\tau^{\text{step}} > 0$ a facet is expected.

Using the perturbation theory of the horizontal interface, it is possible, as mentioned above, to study also the microscopic interfaces associated with the $(\text{step}, \mathbf{m})$ boundary conditions. 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 3. *If the temperature is low enough, i.e., if $\beta \geq \beta_0$, where $\beta_0 > 0$ is a given constant, then the step free energy $\tau^{\text{step}}(\phi)$, defined by limit (64), exists, is strictly positive, and extends by positive homogeneity to a strictly convex function. Moreover, $\tau^{\text{step}}(\phi)$ can be expressed as an analytic function of β, for which a 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 titled by a very small angle θ 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 4. *For $\beta \geq \beta_0$, we have*

$$\partial\tau(\theta,\phi)/\partial\theta\,|_{\,\theta=0^+} = \tau^{\rm step}(\phi) \tag{65}$$

This relation, together with equation (62), implies that one obtains the shape of the facet by means of the two-dimensional Wulff construction applied to the step free energy.

Corollary 1. *The equilibrium crystal presents, if $\beta \geq \beta_0$, a facet orthogonal to the (0,0,1) direction, whose shape is given by*

$$\mathcal{F} = \Big\{\mathbf{x} \in \mathbf{R}^2 : \mathbf{x}\cdot\mathbf{m} \leq \tau^{\rm step}(\mathbf{m}) \ \text{ for every } \ \mathbf{m} \in \mathbf{S}^1\Big\} \tag{66}$$

The reader will find a detailed discussion on these points, as well as the proofs of Theorems 3 and 4, in ref. [14]. A brief explanation of these results can be found in ref. [16].

From the properties of $\tau^{\rm step}$ stated in Theorem 3, 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 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. The conjectured value of β_R, the roughening inverse temperature, is given by $K_R \sim 0.38$ [17]. It is then natural to believe that the equality (65) is true for any β larger than β_R, allowing us to determine the facet shape from Corollary 1, and that for $\beta \leq \beta_R$, both sides in the 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 the above results.

References

[1] C. Rottman, M. Wortis, *Statistical Mechanics of equilibrium crystal shapes: Interfacial phase diagrams and phase transitions*, Phys. Rep. **103**, 59–79 (1984).

[2] H. van Beijeren, I. Nolden, *The roughening transition.*, in W. Schommers, P. von Blackenhagen, eds., "Topics in Current Physics", vol. 43, Springer, Berlin, 1987.

[3] A. Messager, S. Miracle-Sole, J. Ruiz, *Convexity properties of the surface tension and equilibrium crystals*, J. Stat. Phys. **67**, 449–470 (1992).

[4] R.L. Dobrushin, S.B. Shlosman, *Thermodynamic inequalities and the geometry of the Wulff construction*, in S. Albeverio et al., eds., "Ideas and Methods in Mathematical Analysis, Stochastics and Applications", Cambridge University Press, Cambridge, 1992.

[5] J. Bricmont, J.L. Lebowitz, C.E. Pfister, *On the surface tension of lattice systems*, Ann. Acad. Sci. New York **337**, 214–223 (1980).

[6] J.L. Lebowitz, C.E. Pfister, *Surface tension and phase coexistence*, Phys. Rev. Lett. **46**, 1031–1033 (1981).

[7] A.F. Andreev, *Faceting phase transitions of crystals*, Sov. Phys. JETP **53**, 1063 (1981).

[8] D.B. Abraham, J. De Coninck, F. Dunlop, *Contact angle for the 2–d Ising ferromagnet*, Phys. Rev. B **39**, 4708 (1989).

[9] J.E. Avron, H. van Beijeren, L.S. Shulman, R.K.P. Zia, *Roughening transition, surface tension and the equilibrium droplet shapes in a two-dimensional Ising system*, J. Phys. A: Mat. Gen. **15**, L81–L86 (1982).

[10] S. Miracle-Sole, J. Ruiz, *Interface models and boundary conditions*, work in progress.

[11] H.W.J. Blöte, H.J. Hilhorst, *Roughening transition and the zero-temperature triangular Ising antiferromagnet*, J. Phys. A: Mat. Gen. **15**, L631–L637 (1982).

[12] B. Nienhuis, H.J. Hilhorst, H.W.J. Blöte, *Triangular SOS models and cubic crystal shapes*, J. Phys. A: Mat. Gen. **17**, 3559–3581 (1984).

[13] R. Kotecky, S. Miracle-Sole, *Roughening transition for the Ising model on a bcc lattice. A case in the theory of ground states*, J. Stat. Phys. **47**, 773–799 (1987).

[14] S. Miracle-Sole, *Surface tension, step free energy and facets in the equilibrium crystal shape*, J. Stat. Phys. **79**, 183–214 (1995).

[15] J. Bricmont, A. El Mellouki, Fröhlich, *Random surfaces in Statistical Mechanics: Roughening, rounding, wetting,...*, J. Stat. Phys. **42**, 743–798 (1986).

[16] S. Miracle-Sole, *On the microscopic theory of phase coexistence*, in J.J. Brey et al., eds., "25 Years of Non-Equilibrium Statistical Mechanics", Springer, Berlin, 1995.

[17] J.D. Weeks, G.H. Gilmer, H.J. Leamy, *Structural transition in the Ising model interface*, Phys. Rev. Lett. **31**, 549–551 (1973).