Equilibrium Crystal Shape: Two Dimensions and Three Dimensions

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We show that the two-dimensional (2D) equilibrium crystal shape (ECS) determined from the anisotropic step free energy gives the facet shape of the 3D ECS below the roughening temperature. This fact brings us a general and efficient method to obtain the essential feature of 3D ECS, by estimating the step free energy from the 1D solid-on-solid (SOS) model or the 2D Ising model. We apply the method to the body-centered-cubic solid-on-solid (BCSOS) model and obtain almost the exact facet shape for a wide range of temperatures.

Thermal evolution of the equilibrium crystal shape (ECS) has drawn much attention in connection with the roughening transition and its associated faceting transition. Below the roughening transition temperature $T_R$, the ECS of a three-dimensional (3D) crystal is composed of facets and rounded surfaces. Although the critical behavior of the ECS, around $T_R$ and around the facet edge, has been a central subject of study, we would like to stress here that the off-critical ($0 < T < T_R$) behavior of the ECS is also an interesting problem, since in this intermediate temperature region, we have a non-spherical, highly non-trivial ECS reflecting the inherent anisotropy of the system.

Theoretically, although we have an exactly solvable model in a special case, to obtain the finite-temperature ECS is not an easy task, in general. The traditional method is the so-called Wulff construction where full information of the anisotropic interface free energy is needed. Hence, the problem reduces to the calculation of reliable values of interface free energy $\gamma(n, T)$ for all interface directions $n$ and temperature $T$, which is still very difficult in most cases. To the best of our knowledge, the first research along this line was made by Rottman and Wortis, where $\gamma(n, T)$ is calculated numerically by a mean-field-theory-like treatment. Although they obtained many important results, such as the possibility of the first-order transition of the ECS, we should say that their treatment was not sufficiently satisfactory due to its calculational complexity and to the nature of its approximation (mean-field theory).

We should note the following facts: (1) the essential feature of the ECS is given by the shape of facets, and (2) the position of the facet edge is determined by the step free energy. For the point (2), we assume that the transition (facet area→curved area) at the facet edge is continuous (e.g., Pokrovsky-Talapov-Gruber-Mullins type or ‘3/2’-th order). Hence, to have the essential part of the ECS, we should determine the facet shape which needs only the anisotropic step free energy instead of the full interface free energy. This is the basic idea of the method to obtain the overall ECS which we shall present in this letter.

Consider a facet and its adjacent curved surface. We describe the ECS surface using a Cartesian coordinate system $(x, y, z)$ as $z=z(x, y)=z(x)$. The $z$-direction is chosen to be normal to the facet. The orientation of the surface at each position is specified by the two-dimensional vector $p=(p_x, p_y)$ defined by

$$p_x = \frac{\partial z}{\partial x}, \quad \frac{\partial z}{\partial y}. \quad (1a)$$

The ordinary three-dimensional normal vector $n$ is given by $(-p_y, -p_x, 1)$. The ECS, or the
functional form of \( z(x, y) \), is determined from the interface free energy per projected area, which is denoted by \( f(p) \) with \( p = (p_x, p_y) \) being the mean orientation of the interface. The quantity \( f(p) \) is related to the ordinary interface tension (interface free energy per area) \( \gamma(n) \) as

\[
f(p) = \gamma(n) \sqrt{1 + p_x^2 + p_y^2}.
\]  

(2)

Instead of resorting to the classic Wulff construction, we have a ‘modern’ method\(^{20}\) to obtain the ECS from \( f(p) \), which is convenient to derive many important interface properties.\(^{30,31}\) Andreev’s Legendre-transformed free energy \( \tilde{f}(\eta) \), which is defined by

\[
\tilde{f}(\eta) = f(p) - p \cdot \eta,
\]

\( \eta = (\eta_x, \eta_y) \),

(3)

directly gives the ECS through the equation

\[
\tilde{x} = \tilde{f}(-\tilde{x}), \quad \tilde{y} = \lambda \tilde{x},
\]

\[
\tilde{x} = (\tilde{x}, \tilde{y}) = (\lambda x, \lambda y).
\]

(4)

In the above, \( \lambda \) is the Lagrange multiplier corresponding to the volume-fixing constraint. Since we are interested in the shape of a crystal rather than its volume, we shall only consider the normalized ECS given by the equation \( \tilde{x} = \tilde{f}(-\tilde{x}, -\tilde{y}) \). Then, the normalized coordinate \( \tilde{x}(\tilde{y}) \) is identified with \( -\eta, (-\eta) \).

Let us remind ourselves of the following relation associated with the Legendre transformation of the variables \( p \rightarrow \eta \):

\[
\tilde{x} = -\frac{\partial f(p)}{\partial p_x}, \quad \tilde{y} = -\frac{\partial f(p)}{\partial p_y}.
\]

(5)

Noting that the facet edge corresponds to the boundary between the flat area \((p = 0)\) and the curved area \((p \neq 0)\), we have, from eq. (5), a set of equations to determine the shape of the facet edge:

\[
\tilde{x} = -\lim_{|p| \rightarrow 0} \frac{\partial f(p)}{\partial p_x},
\]

\( (6a) \)

\[
\tilde{y} = -\lim_{|p| \rightarrow 0} \frac{\partial f(p)}{\partial p_y}.
\]

(6b)

As for the \( p \rightarrow 0 \) behavior of \( f(p) \), we have the following form of expansion:

\[
f(p) = f(0) + \frac{\gamma_r(\theta)}{d} \cdot |p| + \alpha(\theta) \cdot |p|^\mu + \cdots,
\]

\( (\mu > 1) \)

(7)

where we have introduced the angle parameter \( \theta \) by

\[
p = (-|p| \cos \theta, -|p| \sin \theta),
\]

\[
|p| = \sqrt{p_x^2 + p_y^2}.
\]

(8)

Physically, \( \gamma_r(\theta) \) represents the step free energy,\(^{9,32}\) \( d \) the unit height of the step, \( \theta \) the mean step orientation angle (orientation angle of the normal vector) relative to the \( x \)-axis and \( |p|/d \) the step density. The exponent \( \mu \) in (7) is 3 for most cases, but our argument given below is valid for any value of \( \mu > 1 \). In some cases, the condition \( \alpha(\theta) > 0 \) is required to guarantee the continuous transition at the facet edge. Putting (7) into (6), we obtain

\[
\tilde{x} = \frac{1}{d} \left[ \gamma_r(\theta) \cos \theta - \frac{\partial \gamma_r(\theta)}{\partial \theta} \sin \theta \right],
\]

\( (9a) \)

\[
\tilde{y} = \frac{1}{d} \left[ \gamma_r(\theta) \sin \theta + \frac{\partial \gamma_r(\theta)}{\partial \theta} \cos \theta \right],
\]

(9b)

and

\[
\frac{d\tilde{y}}{d\tilde{x}} = \frac{d\tilde{y}}{d\tilde{x}} = -\cot \theta.
\]

(10)

It should be noted that eqs. (9) and (10) are precisely the equations to determine the 2D ECS where the step free energy \( \gamma_r(\theta) \) plays the role of the 1D interface free energy of a 2D system. Also, the eq. (9) can be regarded as the \( \theta \neq 0 \) generalization of the relation\(^{9,32} \) between the facet edge position and the step free energy.

Thus, we have shown that the facet shape is determined from the step free energy through eq. (9). The next task is to obtain accurate values of the step free energy \( \gamma_r(\theta) \) for all \( \theta \). Since the exact values are not available, in general, we take the following approximation scheme for \( \gamma_r(\theta) \). As the crudest (‘0-th order’) approximation, we adopt the free energy of the 1D SOS (solid-on-solid) model denoted by \( \gamma^{\text{1DOS}}(\theta) \). For higher temperatures, to take the overhang configurations of a step into consideration, we adopt the exact interface free energy of the 2D Ising model denoted by \( \gamma^{\text{Ising}}(\theta) \) as the first-order approximation. The ap-
proximation by $\gamma^{(1D\text{SOS})}(\theta)$ has a merit that it has a wide range of applicability. Moreover, at relatively low (but high enough above absolute zero) temperatures where the overhangs and adatoms are quite rare, we can surely expect that use of $\gamma^{(1D\text{SOS})}(\theta)$ gives a good result. The approximation by $\gamma^{(\text{Ising})}(\theta)$ is much more difficult than that by $\gamma^{(1D\text{SOS})}(\theta)$, but we have still many cases where $\gamma^{(\text{Ising})}(\theta)$ can be evaluated exactly.

As an illustration, we apply the method to the BCSOS (body-centered-cubic solid-on-solid) model, the results are shown in Figs. 1-3. Note that the microscopic energy cost for the formation of a one-length step in the BCSOS model is $J$ in the notation of ref. 9 ($k_B T_r/J \approx 1.44$). Then, the value of coupling constant required to obtain $\gamma^{(\text{Ising})}(\theta)$ for the square lattice Ising model is $J/2$. It is clearly seen that even the crudest approximation using $\gamma^{(1D\text{SOS})}(\theta)$ gives nearly exact facet shape for $k_B T/J \leq 0.5$. The result for $\gamma^{(\text{Ising})}(\theta)$ shows good agreement for $k_B T/J \leq 0.9$. These results demonstrate that our method works excellently for a wide range of $J$. We remark here that, in our recent calculation of the ECS for the 2D absolute SOS model by a newly proposed Monte-Carlo method, the calculated shape and the size of the facet agree with the ones obtained here for $\gamma^{(\text{Ising})}(\theta)$. For $k_B T/J > 0.9$, where the facet shape is almost circular, the approximate facet size falls off from the exact one, even when using $\gamma^{(\text{Ising})}(\theta)$. This can be mainly ascribed to the presence of adatoms. For the BCSOS model, due to the constraint that the nearest neighbor height differences be $\pm 1/2$, the adatoms play the role of impurities which restrict the step wandering and reduce the fluctuations causing the higher transition temperature. In the 2D Ising model, since such an impurity-pinning effect is missing, the transition temperature is lower than that in the BCSOS model. Hence we will have an improved approximation if we take into account the effect of adatoms.

We have shown that the shape of the facet is just the 2D ECS determined from the anisotropic step free energy. We have the following physical interpretation of this fact. The curved area surrounding the facet can be regarded as the assembly of long step loops encircling the facet. Due to the assumption of the continuous transition at the facet edge, we have a vanishing step density close to the facet edge. Hence, the innermost step loop behaves as a free one-dimensional closed interface, which has a shape given by the 2D ECS. This interpretation, however, does not give full account of our result (9); we cannot determine the size of the facet (or corresponding 2D ECS) from this interpretation alone. The Lagrange multiplier $\lambda$ appearing in our equa-

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**Fig. 1.** Thermal evolution of the (100) facet in the BCSOS model obtained from eqs. (6) and (7) in ref. 9, for $k_B T/J = 0.1$ (outermost), 0.3, 0.5, 0.7, 0.9 and 1.1 (innermost). Facet area shrinks to zero at $T_r$ given by $k_B T_r/J = 1/log (1 + \sqrt{2}) (\approx 1.44)$.

**Fig. 2.** Similar figure as Fig. 1 for the approximation by $\gamma^{(\text{Ising})}$. Facet area shrinks to zero at $T_r$ given by $k_B T_r/J = 1/log (1 + \sqrt{2}) (\approx 1.13)$.

**Fig. 3.** Similar figure as Fig. 1 for the approximation by $\gamma^{(1D\text{SOS})}$. 
tion (9) is the same as that in eq. (4), which automatically determines the size of the facet relative to the bulk crystal size.

Since the calculation of interface free energy by the 1D SOS model can be easily performed for various cases, our method to study the thermal evolution of 3D ECS has a wide range of applicabilities. Moreover, going back to eq. (5), the possibility exists whereby the method can be applied even for the cases where the transition at the facet edge is of the first order (i.e., the surface gradient changes discontinuously at the facet edge). Finally, we should like to point out that, in principle, we can make an experimental estimation of the bond energy of a crystal, by observing the thermal evolution of the ECS and comparing it with the theoretical calculation in which our method can be of use.

These are the subjects of future study and will be discussed elsewhere.

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References