Novel Numerical Method
for Studying the Equilibrium Crystal Shape

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A method to calculate the equilibrium crystal shape is presented, which is based on the numerical (Monte-Carlo) evaluation of the Andreev’s Legendre-transformed interface free energy. The method is applied to draw the equilibrium shape of the two-dimensional absolute solid-on-solid models.

Recently, thermal changes of the equilibrium crystal shape (ECS) has drawn much attention, in connection with the roughening transition of the two-dimensional interface. One of the expected shape changes is the faceting transition at the roughening transition temperature $T_R$. It is expected that below $T_R$ the crystal has a finite area of flat surface (= facet) and above $T_R$ the crystal has only curved surface with no facet. Theoretically, it has been predicted that the curvature of the surface has a finite jump with, after a suitable normalization, a universal amplitude (‘universal curvature jump’). The prediction is based on the exact solution of the BCSOS (body-centered-cubic SOS) model[13-15] and on the equivalence between the roughening transition and the Kosterlitz-Thouless type transition. Experimentally, there are both for and against this universal curvature jump.

Below $T_R$, there expected another important change in shape around the facet edge. If we draw the crystal profile in $z$-$x$ plane, then the theory predict that the profile should have the following form:

$$z = 0 \quad (x \leq x_c),$$

$$= -\text{const} \cdot (x-x_c)^\theta, \quad (x > x_c, \theta = 3/2) \quad (1)$$

where $x_c$ represents the position of the facet edge. This type of second order (or 3/2-th order) phase transition is called the Pokrovsky-Talapov-Gruber-Mullins type transition, whose associated exponent ($\theta = 3/2$) contrasts to the ‘classical’ value ($\theta = 2$) of the exponent. To the present authors, existing experimental results do not seem to reach the consensus of this ‘3/2-power’ law but rather seem to be in favor of the classical theory ($\theta = 2$) in the close vicinity of the facet edge. In certain case, a first order transition is also reported. Several explanations for the discrepancy between the theoretical prediction and the experimental results have been suggested (for example, rounding due to finiteness of the crystal size, elastic or curvature energy effect, surface relaxation, etc.) but there seems to be no decisive answer.

In such a situation, reliable calculation, although numerical, of the ECS made on a ideal model system (but more realistic than the BCSOS model) is important. Monte-Carlo simulation for the ECS was first performed by Saito and Uchiuma on the absolute solid-on-solid (ASOS) model and its ‘bi-directional’ extension, adopting the kinetics which (nearly) conserves the total volume of the crystal. They directly obtained the profile of the ECS and, although quantitative estimate of the universal curvature jump was not made, verified a faceting transition at $T_R$. For the facet edge problem, their result supports the classical theory ($\theta = 2$) as do the experimental results.

The purpose of this letter is to propose another numerical method to obtain the ECS. As compared with the approach by the ‘direct
simulation’ for the ECS by Saito and Uchiyama, our approach is somewhat ‘indirect’. But, as will be mentioned later, our present method and its extension are suited for quantitative study of the ECS and has a wide range of applicability.

Our starting point is the Andreev’s re-formulation\(^{25}\) for calculation of the ECS. We draw the ECS in xyz-space as \(z = z(x, y)\). We denote the gradients of the surface at \((x, y, z(x, y))\) by \(p_1\) and \(p_2\), which are given by

\[
\begin{align*}
    p_1 &= \frac{\partial z(x, y)}{\partial x}, \\
    p_2 &= \frac{\partial z(x, y)}{\partial y}.
\end{align*}
\]

(2)

Let us consider a piece of macroscopically flat surface with ‘mean gradients’ \(p_1\) and \(p_2\), and assume that its projection onto the xy-plane forms an \(L \times L\) square. The interface free energy per projected area, i.e. (total interface free energy)/\(L^2\), for this piece of tilted interface is denoted by \(f(p)\). The Andreev’s free energy \(f(\eta)\) is defined through the Legendre-transformation of the variable \(p \rightarrow \eta\):

\[
\begin{align*}
    f(\eta) &= f(p) - \eta \cdot p, \\
    p = p(\eta) &= -\frac{\partial f(\eta)}{\partial \eta},
\end{align*}
\]

(3a, 3b)

where we have denoted \(p = (p_1, p_2)\). The variable \(\eta = (\eta_1, \eta_2)\) plays the role of ‘external field’ to cause the tilt of the interface. The Andreev’s free energy has an important property that, instead of resorting to the Wulff’s theorem,\(^{28,29}\) we can directly calculate the ECS from \(f(\eta)\) through the following equation:

\[
\lambda z = f(-\lambda x).
\]

(4)

In the above, we have denoted \(z = (x, y)\) and the constant \(\lambda\) is the Lagrange multiplier associated with the volume-fixing constraint which depends on the total volume of the crystal. Since we are interested in the ‘shape’ rather than the volume of the crystal, we shall only consider to ECS determined from eq. (4) with \(\lambda = 1\), which we call the normalized ECS. Hence, if we have the Andreev’s free energy for a given model of interface, we automatically have the (normalized) ECS for the model.

Our strategy is to evaluate the Andreev’s free energy by Monte-Carlo method. To calculate the free energy by Monte-Carlo method, we have two ways at hand.\(^{30}\) One is based on the thermodynamical relation \(\langle E \rangle = -\partial F/\partial \beta \) (\(\beta = 1/k_B T\)), between the (averaged) internal energy \(\langle E \rangle\) and the free energy \(F\), from which we have

\[
F(\beta_1) - F(\beta_2) = -\int_{\beta_2}^{\beta_1} \langle E \rangle d\beta.
\]

(5)

This method is simple but practically somewhat awkward since it involves a numerical integration which may cause extra numerical error other than that from the Monte-Carlo evaluation of \(\langle E \rangle\).

The other way, which we adopt here, is the method of distribution function.\(^{31,32}\) Let us remind ourselves of the definition of the energy distribution function \(P(E, \beta)\):

\[
P(E, \beta) = e^{-\beta E} \cdot W(E)/Z(\beta),
\]

(6)

where \(W(E)\) is the density of states and \(Z(\beta)\) is the partition function. Since \(W(E)\) is independent of \(\beta\), the ratio \(Z(\beta_2)/Z(\beta_1)\) is given by

\[
Z(\beta_2)/Z(\beta_1) = \exp \left[ -(\beta_2 - \beta_1)E \right] \cdot P(E, \beta_2)/P(E, \beta_1).
\]

(7)

The quantity \(P(E, \beta)\) is easily calculated by direct Monte-Carlo sampling to make a histogram for \(E\). Practically, to improve the statistics, we calculate a coarse-grained distribution function by counting number of data which fall into the range \([E - \Delta E/2, E + \Delta E/2]\) with suitably chosen value of \(\Delta E\). Putting the calculated \(P(E, \beta)\) into eq. (7) we have

\[
\Delta(\beta F) = \beta_2 F(\beta_2) - \beta_1 F(\beta_1) = (\beta_2 - \beta_1)E - \log \left[ P(E, \beta_1)/P(E, \beta_2) \right].
\]

(8)

This method can be easily extended for the cases where some ‘external variables’, adding to the temperature \(T\), exist. In our case, the external variable is the field \(\eta\) conjugate to the interface gradient vector \(p\).

We tested our method by the one-dimensional (1D) absolute solid-on-solid (ASOS) model for which the exact solution is available. We found a good (within few percent for length = 100 and MCS (Monte-Carlo steps per site) = 10^5) agreement between the exact ECS and the one calculated by the present.
method, which guarantees the reliability of our method. We then apply the method for the 2D-ASOS model with size $L \times L$, whose Hamiltonian is given by

$$H = J \sum_{\langle i,j \rangle} |h_i - h_j| + \eta_1 \cdot \Sigma'(h_{i+2} - h_i)$$
$$+ \eta_2 \cdot \Sigma'(h_{i+1} - h_i).$$  \hspace{1cm} (9)

In the above, the symbol $\Sigma_{\langle i,j \rangle}$ denotes the summation over the nearest neighbor pairs and $\Sigma'(\Sigma')$ denotes the summation over the horizontal (vertical) nearest neighbor pairs. We have also denoted the unit horizontal (vertical) vector by $\hat{x}(\hat{y})$. The lattice spacings are chosen to be unity and the height variables $\{h_i\}$ take only integer values ($-\infty, \cdots, -1, 0, 1, 2, \cdots, \infty$). For convenience, the coupling constant $J$ is chosen to be $J/k_B = 1$. In the actual simulation, we adopt the free boundary condition and we fix the center height $h_{(L/2,L/2)}$ to be zero to remove the artificial degeneracy coming from the invariance of the Hamiltonian under the parallel shift of all heights, $h_i \rightarrow h_i + \Delta h$ (all $i$). To make the energy distribution function, we used $10^7$ MCS data after discarding the first $2 \times 10^4$ thermalization steps, recording the quantities $\Sigma_{\langle i,j \rangle} |h_i - h_j|$, $\Sigma'(h_{i+2} - h_i)$ and $\Sigma'(h_{i+1} - h_i)$ at each step.

In Fig. 1, the profiles of the ECS at $T=0.9$ and $T=1.4$ for $\langle 1 0 0 \rangle$-direction are shown. At $T=0.9$, we find a faceted profile although the facet edge is somewhat smeared out due to finite size rounding effect. From the figure we estimate the edge position $x_c$ to be $x_c = 0.35$, which is slightly lower but is consistent with the value $x_c = 0.38$ calculated from the single step formation stability criterion. At $T=1.4$ we have a curved profile with no facet. Hence, we can expect the faceting transition temperature between $T=0.9$ and $T=1.4$, which is consistent with the recent estimate of the roughening temperature $T_R = 1.24$ for 2D-ASOS model. In Fig. 2, we show the over-all ECS for the 2D-ASOS model at $T=0.9$ calculated by our method. In Fig. 3, we draw the corresponding contour map of the ECS, after a suitable interpolation between the actually calculated data points. In the figure, an almost circular facet with radius $0.35$ is observed. This is also consistent with the expected facet shape.

To conclude, we have proposed a new numerical method to obtain the equilibrium crystal shape (ECS). As an illustration, we have applied the method to the two-dimensional absolute solid-on-solid (ASOS) model.

Fig. 1. The normalized ECS of $\langle 1 0 0 \rangle$ direction for the 2D-ASOS model (eq. (9)), where $\Delta z(x,0) = z(x,0) - z(0,0)$. The filled (unfilled) circles are the results of MC calculation made at $T=0.9$ ($T=1.4$) with $32 \times 32$ system size. The ECS at $T=1.4$ has no facet, while the ECS at $T=0.9$ has a facet whose edge lies around $x = 0.35$.

Fig. 2. The over-all normalized ECS calculated for the 2D-ASOS model ($size = 32 \times 32$, $T=0.9$). The enlightened spheres correspond to the facet.

Fig. 3. The contour map of the normalized ECS at $T=0.9$. Relative height difference between the neighboring contour lines is $5.696 \times 10^{-3} = |z(0.5, 0.5) - z(0, 0)|/16$. The authors thank Mr. T. Irisawa for his help in drawing this figure.
We have observed a change (faceted$\rightarrow$non-faceted) in the crystal shape through a temperature, which confirms the faceting transition for the model.

Our numerical method based on the Andreev's free energy has a wide range of applicability. For example, we can apply the method to non-SOS type interface models such as the domain walls in the Ising models with twisted boundary condition. Further, the quantum interface can be treated by our method using the quantum Monte-Carlo technique. These are now under study and will appear in future publications.

In this letter, we have restricted ourselves to studying over-all properties of the ECS for the ASOS models. For detailed quantitative study of the ECS, it is important to examine 'differential' quantities such as gradients and curvature. It is of course possible to obtain these quantities from the calculated ECS by numerical differentiation but the precision will not be good enough. Instead, as an extension of the present method, we have recently found an effective way to calculate the curvature of the ECS. The results of its application, in particular, to the universal curvature jump at $T_R$ and to the profile around the facet edge, will be published in a separate paper.\textsuperscript{37}

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References