Non-universal equilibrium crystal shape results from sticky steps

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Abstract

The anisotropic surface free energy, Andreev surface free energy and equilibrium crystal shape \( z(x, y) \) are calculated numerically using a transfer matrix approach with the density matrix renormalization group (DMRG) method. The adopted surface model is a restricted solid-on-solid (RSOS) model with ‘sticky’ steps, i.e. steps with a point-contact-type attraction between them (p-RSOS model). By analyzing the results, we obtain a first-order shape transition on the ECS profile around the (111) facet; and on the curved surface near the (001) facet edge, we obtain shape exponents having values different from those of the universal Gruber–Mullins–Pokrovsky–Talapov (GMPT) class. In order to elucidate the origin of the non-universal shape exponents, we calculate the slope dependence of the mean step height of ‘step droplets’ (bound states of steps) \( \langle n(p) \rangle \) using the Monte Carlo method, where \( p = (\partial z/\partial x, \partial z/\partial y) \) and \( \langle \cdot \rangle \) represents the thermal average. Using the result of the \( |p| \) dependence of \( \langle n(p) \rangle \), we derive a \( |p| \)-expanded expression for the non-universal surface free energy \( f_{\text{eff}}(p) \), which contains quadratic terms with respect to \( |p| \). The first-order shape transition and the non-universal shape exponents obtained by the DMRG calculations are reproduced thermodynamically from the non-universal surface free energy \( f_{\text{eff}}(p) \).

1. Introduction

The surface free energy is one of the most fundamental quantities in surface science. The equilibrium crystal shape (ECS) (figure 1) is the shape of a crystal particulate with minimum surface free energy under equilibrium conditions [1–13]. A polyhedral ECS is obtained using the Wulff theorem from a polar graph of the anisotropic surface free energy through the Wulff construction. An ECS with several facets and curved areas is obtained using the Landau–Andreev method [7, 8] and this ECS is found to be similar to the Andreev surface free energy, where the work associated with step formation is eliminated from the surface free energy per projected area [8]. Since the ECS reflects the anisotropy of the surface free energy, studying the ECS corresponds to studying the surface free energy itself.

Recently, we applied the restricted solid-on-solid (RSOS) model coupled with the Ising system (RSOS-I model) [14–16] to investigate the interplay between surface steps and adsorbates on a vicinal surface. The RSOS model [17] (figures 1 and 2) is an SOS (or Kossel crystal) [18, 19] model in which differences in height between nearest-neighbor (nn)
surface sites are restricted to \([0, \pm 1]\). From statistical mechanical calculations using the RSOS-I model, a first-order shape transition is found to occur on the ECS profile. In addition to the shape transition, the ‘shape exponent’ on the ECS seems to have values different from the universal Gruber–Mullins–Pokrovsky–Talapov (GMPT) or one-dimensional (1D) free fermion values [20–32].

Concerning the universal behavior of the GMPT, the universal form of the free energy is understood in terms of the terrace-step-kink (TSK) picture [20–23] (figure 1) for a vicinal surface as follows:

\[
\langle f(\rho) = f(0) + \gamma \rho + B \rho^3 + O(\rho^4), \quad (1)
\]

where \(\rho\) represents the step density, \(\gamma\) represents the step tension and \(B\) represents the step interaction coefficient. A many-body system of non-overlapping linear excitations embedded in two dimensions is known to have the form of free energy as expressed in equation (1). The TSK picture has been confirmed by exact calculations of the free energy using a microscopic body-centered cubic solid-on-solid (BCSOS) model [24, 25]. Experimentally, the universal behavior expressed by equation (1) has been confirmed by observations of the ‘shape exponent’ on the ECS profile [33–48]. The ECS near a facet is expressed by \(|z(x, y) - z(x_c, y_c)| = A|x - x_c|^{3/2}\), where \((x_c, y_c)\) are the coordinates of the facet contour, the power on the right-hand side is the shape exponent in the normal direction \(\theta_n\) and \(A\) is the ‘amplitude’. From equation (1), and following some thermodynamic calculations, the value of \(\theta_n\) is obtained as 3/2, which is a GMPT universal value.

In addition, based on recent developments in the study of non-equilibrium bunched steps [49–53], the values of the exponents in the profile of a bunched step are related to the force range of the effective step–step interactions on the non-equilibrium vicinal surface. The values of the exponents are thought to be related to the shape exponent \(\theta_n\) on the ECS. From these perspectives, the importance of studying the shape exponent is increasing.

In order to establish the non-GMPT shape exponent on the ECS, a \(\rho\)-expanded expression for surface free energy with non-GMPT terms should be derived. In our previous work [15], we demonstrated the appearance of a short-range step–step attraction mediated by adsorbates, and we introduced the step-droplet picture [15]. Due to the complexity of interplay between surface steps and adsorbates, however, we could not derive a \(\rho\)-expanded expression for the non-GMPT surface free energy.

The aim of the present paper is to establish the non-GMPT shape exponent on the ECS. In other words, the purpose is to find a mechanism to obtain a \(\rho\)-expanded expression for surface free energy with non-GMPT terms in a system with a short-range step–step attraction.

To obtain clear results, we present a simple model: the RSOS model with a point-contact-type step–step attraction (p-RSOS model) [54, 55]. Physically, the step–step attraction represents the transient bond formed by the spatial overlap of orbitals between atoms at the collision point of the adjacent steps (figure 2(b)).

This paper is organized as follows. In section 2, we present the definition of the p-RSOS model and show statistical mechanical calculations on the ECS, the equilibrium facet shape and the non-universal shape exponents. In section 3, a study on step droplets near equilibrium is described. Calculation of the mean step height of the step droplets \(n\) is carried out using a Monte Carlo method. In section 4, we derive a \(\rho\)-expanded expression for the vicinal surface free energy, which contains non-GMPT terms. In section 5, using the non-GMPT vicinal surface free energy, we thermodynamically reproduce the results for the p-RSOS model obtained by the transfer matrix method in section 2. In section 6, we present a summary and discussion. Finally, a conclusion is given in section 7.

2. Statistical mechanical calculations using the p-RSOS model

2.1. Model Hamiltonian

Let us consider the surface height \(h(i, j)\) at a site \((i, j)\) on a square lattice to describe surface microscopic undulations (figure 2). In the RSOS model [17], the height differences between nn sites are restricted to values of \([1, 0, -1]\). We consider a point-contact-type microscopic step–step
interaction and refer to this model as the p-RSOS model. The Hamiltonian for the p-RSOS model can then be written as
\[ H_{\text{p-RSOS}} = \sum_{i,j} \epsilon \{ |h(i+1,j) - h(i,j)| + |h(i,j+1) - h(i,j)| \} \]
\[ - \epsilon \{ \delta(|h(i+1,j) - h(i,j)|, 1) + \delta(|h(i+1,j) - h(i,j)|, 2) \}, \]
where \( \epsilon \) is the microscopic edge energy, \( \epsilon_{\text{int}} \) is the microscopic step-step interaction energy and \( \delta(a, b) \) is Kronecker’s delta. The summation with respect to \((i,j)\) is performed over all sites on the square lattice. The RSOS restriction is required implicitly. In the case of \( \epsilon_{\text{int}} < 0 \), the interaction among steps becomes attractive.

For a vicinal surface, we add the terms of the Andreev field \( \eta = (\eta_x, \eta_y) \) to the Hamiltonian equation (2) as an external field. The model Hamiltonian given in equation (2) for the vicinal surface then becomes
\[ H_{\text{vicinal}} = H_{\text{p-RSOS}} - \eta_x \sum_{i,j} [h(i+1,j) - h(i,j)] \]
\[ - \eta_y \sum_{i,j} [h(i,j+1) - h(i,j)]. \]

The partition function \( Z \) for the p-RSOS model is given by
\[ Z = \sum_{\{h(i,j)\}} e^{-\beta H_{\text{vicinal}}} \]
where \( \beta = 1/k_B T \), \( k_B \) is the Boltzmann constant and \( T \) is the temperature. The Andreev surface free energy \( f(\eta) \) is the thermodynamic potential calculated from the partition function \( Z \) using
\[ \beta f(\eta) = - \lim_{N \to \infty} \frac{1}{N} \ln Z, \]
where \( N \) is the number of lattice points on the square lattice. In practice, calculation of equation (5) is not an easy task, because the entropy associated with the vast variety of zigzag structures of a surface step and by the parallel movement of steps is difficult to estimate.

Recently, the numerical renormalization group method for 1D quantum spin systems has been further developed to become the density matrix renormalization group (DMRG) method [56–58]. Though the method is approximate and numerical, it successfully reproduces known exact results with high precision. One means of extending the DMRG method to classical systems is by mapping a two-dimensional (2D) classical system to a 1D quantum spin system [59] by use of the transfer matrix [60] together with the Suzuki–Trotter formula [61]. Such a method was developed by Nishino et al for an infinite lattice, and is called the product wavefunction renormalization group (PWFGRG) method [62–64]. For the calculations in the present paper, we also adopt the PWFGRG method.

In order to apply the PWFGRG method to the p-RSOS system, we construct the transfer matrix \( \tilde{T}(t_1, t_2, \ldots, t_N; s_1', s_2', \ldots, s_N') \) (figure 3(a)) using a 19-vertex model [65, 59] (figure 4). The partition function \( Z \) (equation (4)) is then rewritten in terms of \( \tilde{T} \) as
\[ Z = \text{Tr}[\tilde{T}(t_1, t_2, \ldots, t_N; s_1', s_2', \ldots, s_N')^M] \]
where \( N \) is the number of linked vertices and \( M \) is the length of the system in the vertical direction in figure 3(b). The statistical weight of each vertex is shown in figure 5. For a vicinal surface, the statistical weight is multiplied by \( \exp[\beta((t+s')\eta_x + (s+t')\eta_y)/2] \) with \( s, t, s', t' \) having values of \( \{0, \pm 1\} \). Then, by use of the statistical weight denoted by \( V(s, t; s', t') \), the transfer matrix is expressed as follows.
In the limit $M, N \to \infty$, only the largest eigenvalue of the transfer matrix $\Lambda(N)$ contributes to the partition function. The Andreev surface free energy, therefore, is obtained from equation (5) as

$$\tilde{\beta f} = -\lim_{M,N \to \infty} \frac{1}{NM} \ln \Lambda(N)^M.$$  (8)

The transfer matrix is diagonalized efficiently using the PWFRG method. In the PWFRG calculation, the number of so-called ‘retained bases’ $m$ is set from 7 to 37. The number of iterations for the diagonalization process is set to $200-10^4$.

We also calculate the surface gradient $p = (p_x, p_y) = (\partial z/\partial x, \partial z/\partial y)$ using the PWFRG method, where the surface gradient is defined as the thermal average of the height differences as follows:

$$p_x(q) = \langle h(m + 1, n) - h(m, n) \rangle / \alpha_x,$$

$$p_y(q) = \langle h(m, n + 1) - h(m, n) \rangle / \alpha_y.$$  (9)

Here, $\langle \rangle$ represents the thermal average, and $\alpha_x$ and $\alpha_y$ represent the lattice constants in the $x$ and $y$ directions, respectively ($d = \alpha_x = \alpha_y = 1$). By sweeping the field $\beta \eta$, we obtain curves for $p_x$ versus $\beta \eta_x$ or $p_y$ versus $\beta \eta_y$ [14, 15, 32, 54, 55, 65].

Figure 6. Perspective views of the reduced ECS around the (001) facet calculated by the transfer matrix method with the PWFRG algorithm. ($\beta \epsilon)^{-1} = k_B T/\epsilon = 0.3$. (a) p-RSOS model ($\epsilon_{\text{int}}/\epsilon = 0.5$). (b) The original RSOS model ($\epsilon_{\text{int}} = 0$).

2.2. First-order shape transition on the ECS profile

In figure 6, we show perspective views of the calculated Andreev surface free energy $\tilde{f}(\eta)$ divided by $k_B T$ around the (001) surface for $k_B T/\epsilon = 0.3$. From the thermodynamics of the ECS, the Andreev surface free energy and the Andreev field are related to the ECS coordinates $[7, 8]$ by

$$\tilde{f}(\eta_x, \eta_y) = \lambda z(x, y), \quad \eta_x = -\lambda x, \quad \eta_y = -\lambda y,$$

$$p_x = -\frac{\partial \tilde{f}(\eta)}{\partial \eta_x}, \quad p_y = -\frac{\partial \tilde{f}(\eta)}{\partial \eta_y},$$  (10)

where $\lambda$ is the Lagrange multiplier relating to the volume of the particulate. Equation (10) implies that the surface shape of $\tilde{f}(\eta_x, \eta_y)$ is similar to the ECS. We now introduce a reduced ECS $Z = (X, Y)$ such that $Z = \beta \tilde{f}(\eta_x, \eta_y) = \lambda \beta z(x, y)$, $X = \beta \eta_x = -\lambda \beta x$ and $Y = \beta \eta_y = -\lambda \beta y$.

In the case of $\epsilon_{\text{int}} < 0$ (attractive step–step interaction), large [111] facets appear in addition to the (001) facet and the (101) facets, because the (111) surface is energetically stabilized by $\epsilon_{\text{int}}$. For comparison, we show the reduced ECS for the original RSOS model ($\epsilon_{\text{int}} = 0$) calculated by the PWFRG method in figure 6(b).

Along the line $\overline{PP}$ shown in figure 7, we display the temperature dependence of the profile of the reduced ECS in figure 8. As seen from the figure, the (001) facet ends at $(X_c, Y_c)$ and the curved region between the (001) and (111)
2.3. Equilibrium facet shape

The step tension (or the interface tension) $\gamma(\phi)$ between the (001) and (111) surfaces on the ECS for $k_B T/\epsilon = 0.3$ and 0.361, respectively. They are approximately calculated by the following equation:

$$Y = -X + \beta(2\epsilon + \epsilon_{int}).$$

The facet shape obtained by the PWFRG calculations for $k_B T/\epsilon = 0.3$ agrees well with the 2D ECS for the 2D nn Ising model except for the part truncated by the intersection line between the (001) and (111) surfaces.

The step tension (or the interface tension) $\gamma(\phi)$ is given by [32] (equation (C.2))

$$\beta \gamma(\phi) = X_c \cos \phi + Y_c \sin \phi.$$
Therefore, the agreement between the EFS and the 2D ECS for the 2D Ising model also implies an agreement between the step quantities such as the step tension and the step stiffness $\gamma(\phi) = \gamma(\phi) + \partial^2 \gamma(\phi)/\partial \phi^2$ for the RSOS model and the interface quantities such as the interface tension and the interface stiffness for the 2D Ising model [66] appendix A.

For $T < T_f$, the first-order shape transition occurs at the (001) facet edge. In this case, a 'step' actually corresponds to a 'giant step' with a height $nd$ $(d = 1)$. In the large step-height limit, $\ln \epsilon = n \ln(\pi/4)/n$ converges to $\sqrt{2}(\epsilon + \epsilon_{\text{int}})/2$, which is smaller than $\gamma(\pi/4)_{\text{Ising}}$.

Let us now calculate the approximate value of $T_f$, for $T < T_f$, the EFS has the shape of the rounded square truncated by the intersection line between the (001) and (111) surfaces, which is expressed by equation (12). For $T = T_f$, this line contacts the EFS at $(X^*, Y^*)$ as the tangent line. Then, from equations (11) and (12), we have

$$\frac{\cosh^2(\epsilon/k_B T_f)}{\sinh(\epsilon/k_B T_f)} = 2 \cosh \left(\frac{2\epsilon + \epsilon_{\text{int}}}{2k_B T_f} \right).$$

By solving equation (14), we obtain $\epsilon/k_B T_f \approx 2.78778$ or $k_B T_f/\epsilon \approx 0.358709$, which is consistent with the PWFRG calculated value of $k_B T_f/\epsilon$ (section 2.2).

2.4. Non-universal shape exponents

Let us assign $r$ and $\phi_0$ to the line $\overrightarrow{PP}$ for $X > X_c$ so that $X = X_c + r \cos \phi_0$ and $Y = Y_c + r \sin \phi_0$, where $\phi_0 = \pi/4$ is the tilt angle of the line $\overrightarrow{PP}$ at $(X_c, Y_c)$ relative to the crystal axes (figure 7(b)). The 'normal shape exponent' $\theta_n$ is defined as the shape exponent [32] along $\overrightarrow{PP}$ on the ECS profile such that $|Z(X(t), Y(t)) - Z(X_c, Y_c)| = A_0(\phi_0) r^{\theta_n}$ $(0 \leq r)$, where we refer to the coefficient $A_0(\phi_0)$ as the 'normal amplitude'. Similarly, the 'tangential shape exponent' $\theta_t$ and the 'tangential amplitude' $A_t(\phi_0)$ along $\overrightarrow{QQ}$ are defined such that $|Z(X(t), Y(t)) - Z(X, Y_c)| = A_t(\phi_0) |t|^{\theta_t}$, where $t$ is a parameter assigned to the line $\overrightarrow{QQ}$ as follows: $X = X_c - t \sin \phi_0$ and $Y = Y_c + t \cos \phi_0$. Recalling that $\phi_0 = \pi/4$, we express $p_r$ and $p_t$ in terms of $\phi_0$, $p_t$ as follows:

$$p_r = \sqrt{2} p_x, \quad p_t = (p_y - p_x)/\sqrt{2}.$$

We show the logarithm of $p_r$ and $p_t$ in figures 11(a) and (b), respectively.

First, we study the shape exponents for $k_B T/\epsilon = 0.36$, which is an example of $T_f < T < T_f$. By fitting the data in the range $-7.8 < \ln |r/\sqrt{2}| < -6.5$ in figure 11(a) to the linear function $A_0 + A_1 \ln |r/\sqrt{2}|$ by the least-squares method, we obtain $A_0 = 0.98 \pm 0.03$ and $A_1 = 4.3 \pm 0.2$. Similarly, by fitting the data in the range $-4.75 < \ln |t/\sqrt{2}| < -4$ in figure 11(b) to $A_0' + A_1' \ln |t/\sqrt{2}|$, we obtain $A_1' = 2.96 \pm 0.08$ and $A_0' = 4.4 \pm 0.2$. These values give the shape exponents and amplitudes as $\theta_r = 1.98 \pm 0.03$, $\theta_t = 3.96 \pm 0.08$, $A_0(\pi/4) = 40.6 \pm 0.2$ and $A_0(\pi/4) = 7.2 \pm 1.0$.

Both exponents disagree with the GMPT universal values of $\theta_n = 3/2$ and $\theta_t = 3$ [32]. Consequently, we conclude that the profile near the (001) facet contour for $T_f < T < T_f$ and $\phi_0 = \pi/4$ shows non-GMPT behavior in the limit $p_r, p_t \to 0$.

Next, we study the shape exponents for $k_B T/\epsilon = 0.37$, which is an example of $T > T_f$. As seen from figure 11(a), the slope of $\ln p_r$ crosses over from the larger value to the smaller value as $\ln r$ decreases. In figure 11(a), the dashed line represents $\ln p_r = 0.5 \ln |r/\sqrt{2}| - 0.088$ and this line is determined by fitting to the three lowest points. Therefore, in the limit $r \to 0$, we have $\theta_r = 1.5$ and $A_0(\pi/4) = 0.73 \pm 0.04$.

For $p_t$, we fitted the data in the range $-5 < \ln |t/\sqrt{2}| < -4.3$ to $A_0' + A_1' \ln |t/\sqrt{2}|$ and obtained $A_1' = 1.8 \pm 0.3$ and $A_0' = -0.79 \pm 0.08$. These values lead to $\theta_t = 2.8 \pm 0.3$ and $A_0(\pi/4) = 0.062 \pm 0.018$.

From the values of $\theta_r$ and $\theta_t$ for $k_B T/\epsilon = 0.37$, we conclude that the profile near the (001) facet contour for $T > T_f$ and $\phi_0 = \pi/4$ behaves like the GMPT universal profile in the limit $p_r, p_t \to 0$.

We obtain the GMPT amplitudes using the equations [32]

$$A_0(\phi_0) = \frac{2\sqrt{2\beta} \gamma(\phi_0)}{3\pi}, \quad A_t(\phi_0) = \frac{1}{3\pi\beta \tilde{\gamma}(\phi_0)},$$

where we use the universal relation [29]

$$\beta B(\phi_0) = \pi^2/|6\beta \tilde{\gamma}(\phi_0)|.$$

In the temperature region $T > T_f$, from the results shown in section 2.3, the step quantities of a single step are found to be well described by the interface quantities of the 2D nn Ising model. The exact expressions for the interface tension $\gamma(\phi)$ and the interface stiffness $\tilde{\gamma}(\phi)$ in the 2D nn Ising model for the case of $\phi_0 = \pi/4$ are as follows [66, 67, 28] (equation (A.4))

$$\beta \gamma(\frac{\pi}{4})_{\text{Ising}} = \sqrt{2} \cosh^{-1} \left[ \frac{\cosh^2(\beta \phi)}{2 \sinh(\beta \phi)} \right],$$

$$\beta \tilde{\gamma}(\frac{\pi}{4})_{\text{Ising}} = \sqrt{2} \tanh \left[ \beta \gamma(\frac{\pi}{4})_{\text{Ising}} / \sqrt{2} \right].$$
For $k_B T/\epsilon = (\beta \epsilon)^{-1} = 0.36$, we have $\beta \gamma (\pi/4)_{\text{Ising}}/\sqrt{2} \approx 2.08075$ and $\beta \tilde{\gamma} (\pi/4)_{\text{Ising}} \approx 1.371$, and at $k_B T/\epsilon = 0.37$, we have $\beta \gamma (\pi/4)_{\text{Ising}}/\sqrt{2} \approx 2.0051$ and $\beta \tilde{\gamma} (\pi/4)_{\text{Ising}} \approx 1.364$. Using these values for the interface stiffness, we can obtain the GMPT amplitudes from equation (16).

In figure 12, we show $p_x(r)$ along the normal line $\overline{PP}$. The solid curve in figure 12 shows $p_x(r)$ calculated from equation (15) together with the GMPT amplitude determined using equation (16). As seen from the figure, the solid curve disagrees with the values calculated by the PWFRG method not only for $k_B T/\epsilon = 0.36$ (figure 12(a)) but also for $k_B T/\epsilon = 0.37$ (figure 12(b)). For $k_B T/\epsilon = 0.36$, with $p_r < 0.08$, fitting the values obtained by the PWFRG method to $p_x = A_0 + A_1 X$ gives $A_0 = 167.3 \pm 0.3$ and $A_1 = 80.4 \pm 0.2$. This is shown as the broken line in figure 12(a). For $k_B T/\epsilon = 0.37$, the dashed line in figure 12(b) represents $p_x \approx 0.9154 \sqrt{X - X_c}$, based on the value of $A_0$ obtained from the straight line in figure 11(a). The curve agrees with $p_x$ calculated by the PWFRG method for small $X - X_c$.

2.5. Vicinal surface tilted toward the (100) direction

Let us now consider the profile along the curve $\overline{OP}$ in figure 13(a). We show the calculated Andreev surface free energy and the $p_r$--$X$ curve in figures 13(b) and (c), respectively. For $\phi_0 = 0$, we obtain $p_r$ and $p_x$ from equations (10) and (16) and the GMPT universal shape exponents as

$$p_x = \frac{\sqrt{2} \beta \tilde{\gamma}(0)}{\pi} \frac{(X - X_c)^{1/2}}{y}|_{Y = 0}, \quad (19)$$

$$p_y = \frac{1}{\pi \beta \tilde{\gamma}(0)} \frac{Y^2}{x} |_{X = X_c},$$

where $Y_c = 0$ and $X_c = 4.9865 \pm 0.0005$. The interface tension and stiffness in the Ising model are obtained exactly from equations (13) and (A.4) as follows:

$$\beta \gamma(0)_{\text{Ising}} = \cosh^{-1} \left[ \frac{\cosh^2(\beta \epsilon) - 1}{\sinh(\beta \epsilon)} \right], \quad (20)$$

$$\beta \tilde{\gamma}(0)_{\text{Ising}} = \sinh \left[ \frac{\beta \gamma(0)_{\text{Ising}}}{\beta \epsilon} \right].$$

The value of $X_c$ agrees well with $\beta \gamma(0)_{\text{Ising}}$. $p_x$ calculated using equations (19) with (20) is plotted as the dashed line in figure 13(c) and it can be seen that it closely matches the $p_r$--$X$ curve calculated by the PWFRG method for small $p_r$.

Therefore, we conclude that the vicinal surface tilted toward the (100) direction shows typical GMPT universal behavior.

3. Origin of non-universal behavior: step droplets

3.1. Vicinal surface free energy

When the surface slope is chosen to be an external variable instead of the Andreev field $\eta$, the thermodynamic function
of the surface becomes the vicinal surface free energy \( f(p) \). Using the relationship between the Andreev surface free energy and the vicinal surface free energy [8], we obtain \( f(p) \) from \( \tilde{f}(\eta) \) as

\[
f(p) = \tilde{f}(\eta) + \eta \cdot \mathbf{p}.
\]

(21)

Namely, using the notations of the reduced ECS, we have

\[
\beta f(p) = Z + Xp_x + Yp_y.
\]

(22)

In figure 14(a), \( f(p) \) in the p-RSOS model \((\epsilon_{\text{int}}/\epsilon = -0.5)\) calculated by equation (22) is shown and \( f(p) \) in the original RSOS model is shown in figure 14(b). For \( k_B T/\epsilon = 0.3 \), only \( f(0, 0) \) and \( f(1, 1) \) are obtained by the PWFRG calculations, because a vicinal surface with a regular train of steps in the region \( 0 < p < 1 \) is thermodynamically unstable. For \( k_B T/\epsilon = 0.36 \), a \( f(p) \) curve is obtained in the region \( 0 \leq p_x \leq 0.349 \) and a curve for the metastable state in the region \( 0.349 < p_x < 0.501 \). For \( k_B T/\epsilon = 0.3 \) and 0.36, \( f(1, 1) = 2\epsilon + \epsilon_{\text{int}} \).

3.2. Thermal step bunching

The first-order shape transition on the ECS profile around the \((111)\) facet (figure 15(b)) leads to the coexistence of two surfaces in equilibrium (figure 15(a)) [15, 16, 54], and we refer to this process as thermal step bunching [14, 15]. Let us consider the free energy \( \tilde{f}(p) (p = \bar{p}) \) along \( PP \) in figure 7 for a mixture of surfaces with slopes of \( p_0 \) and \( p_1 \) so that the mean slope is \( p \), as shown in figure 15(c). The free energy of the simple mixed system is described as

\[
\tilde{f}(p) = \bar{x}f(p_1) + \bar{x}_0f(p_0), \quad \bar{x} + \bar{x}_0 = 1, \quad (23)
\]

where \( \bar{x}_0 \) and \( \bar{x}_1 \) represent the fractional areas of the surfaces with slopes of \( p_0 \) and \( p_1 \), respectively. Since \( \bar{x}_0 = (p - p_1)/(p_0 - p_1) \) and \( \bar{x}_1 = (p_0 - p)/(p_0 - p_1) \), \( f(p) \) can be rewritten as

\[
\tilde{f}(p) = f(p_1) + \frac{[f(p_0) - f(p_1)]}{p_0 - p_1} (p - p_1). \quad (24)
\]

Equation (24) describes the cotangent line which contacts \( f(p) \) at points \((p_0, f(p_0))\) and \((p_1, f(p_1))\) (figure 15(a)). For \( p_1 < p < p_0 \), therefore, the free energy of the mixed surfaces is lower than that for a homogeneous surface. Moreover, since \( R = \beta \partial \tilde{f}(p)/\partial p \), equation (24) is equivalent to \( Z(R_q) = \beta \tilde{f}(R_q) = \beta \tilde{f}(p) - R_q\beta = \beta \tilde{f}(R)|_{R_q=R_q'-+} \), where \( \beta = 1/k_B T \) (figure 15(b)).

3.3. Mean step height

3.3.1. Giant steps: \( T < T_{f2} \). We consider that the origin of the non-GMPT shape exponents is the formation of local ‘step droplets’ [14, 15], similar to the formation of clusters in a gaseous system near the transition temperature. In order to form a clear image of such step droplets, we investigate the step dynamics near equilibrium using a Monte Carlo method for a vicinal surface tilted towards the \((110)\) direction at low temperature.

Initially, steps numbering \( N_{\text{step}} \) are spaced evenly on a surface with an area of \( 240\sqrt{2} \times 240\sqrt{2} \) (figure 16(a)). The left side of the image is higher than the right side by an amount

![Figure 14](image14.png)

**Figure 14.** Surface free energy per projected area \( f(p) \) (vicinal surface free energy). (a) p-RSOS model, \( \epsilon_{\text{int}}/\epsilon = -0.5 \). \( p_x = p_y = p \). Solid line: \( f(p, p) \) at \( k_B T/\epsilon = 0.36 \). Dashed line: \( f(p, p) \) at \( k_B T/\epsilon = 0.36 \) for the metastable state. Open circle: \( f(1, 1) \) at \( k_B T/\epsilon = 0.36 \). Open squares: \( f(0, 0) \) and \( f(1, 1) \) at \( k_B T/\epsilon = 0.3 \). (b) The original RSOS model \((\epsilon_{\text{int}} = 0)\). Solid line: \( f(p, p) \) at \( k_B T/\epsilon = 0.3 \).

![Figure 15](image15.png)

**Figure 15.** Thermal step bunching and coexistence of two surfaces. (a) Schematic diagram of vicinal surface free energy \( f(p) \equiv f(p, p) \). Filled circle: \( f(p_0) = f(1) \). Dashed line: tangential line connecting \((p_1, f(p_1))\) and \((p_0, f(p_0))\) with a slope of \( R_q \) (equation (24)) [15]. (b) Schematic diagram of the profile of the reduced ECS. \( R = \sqrt{x^2 + y^2} \). Dashed line: shape in the metastable state. The \((111)\) facet edge, where the first-order transition occurs, is indicated by \( R_q \). A surface with a slope \( p_0 \) coexists with a surface with a slope \( p_1 \) at \( R_q \). (c) Step bunching when two surfaces coexist. Dotted line: mean surface slope (=p). Dashed line: local surface with slope \( p_1 \).
equal to $N_{\text{step}}$. Periodic boundary conditions are imposed in the vertical direction in figure 16.

To study the time evolution of the step configuration, we adopt a simple Metropolis algorithm without any driving force to simulate crystal growth. We randomly choose a site $(i, j)$ and allow its height $h(i, j)$ to increase or decrease with equal probability. Then, if the RSOS restriction is satisfied, the height is updated by the Metropolis algorithm with a probability $P$ described by

$$P = \begin{cases} 1 & (\Delta E(i, j) \leq 0), \\ \exp[-\beta \Delta E(i, j)] & (\Delta E(i, j) > 0), \end{cases}$$

(25)

where $\Delta E(i, j) = E(h(i, j) \pm 1) - E(h(i, j))$. The energy $E(h(i, j))$ is calculated using the p-RSOS Hamiltonian shown in equation (2).

In the present Monte Carlo simulation, only non-conserved attachments and detachments of atoms are taken into consideration. Other effects that occur on a real surface are ignored, such as surface diffusion [3], electromigration [72–74], the Schwoebel effect [75, 76], impurity effects [77–79], strain effects [80–84] and the effect of surfactants [85, 86].

For $T < T_{f,2}$, figure 16 shows the formation of giant steps, similar to ‘step faceting’ [87, 4]. As mentioned in our previous paper [55], at sufficiently low temperatures, step unzipping occurs (figure 16(b)), whereas step unzipping seldom takes place. The zipping process corresponds to successive sticking together of steps, starting from the colliding point of adjacent steps, similar to the action of a zip fastener. At slightly higher temperatures where unzipping occurs more frequently, the vicinal surface reaches an equilibrium configuration (figure 16(c)). All the steps join together to form a single giant step, whose edge has the appearance of a smooth (111) surface.

3.3.2. Step droplets: $T_{f,2} < T \leq T_{f,1}$. In this temperature regime, the fluctuations on the step meandering become larger. A snapshot of the surface for $k_B T/\epsilon = 0.36$ is shown in figure 17. In contrast to the low temperature surface structure, giant steps are seen to exist locally, and become larger and smaller dynamically. We refer to such local giant steps as ‘step droplets’. Based on the structure of giant steps at low temperature, we now use Monte Carlo simulations to determine the size of step droplets and the mean number of steps $\langle n \rangle$ contained in giant steps.

In order to calculate $\langle n \rangle$, we divide the square lattice into two sublattices, which are represented by open circles and closed circles in figure 18, respectively. Sweeping $i$ from left to right for fixed $j$ on the A sublattice, we define the beginning of a step droplet at $(i, j)$ as the position where successive height changes begin to occur. If these successive height changes begin at $(i + n, j)$ in the A sublattice, the size of the step droplet is taken to be $n(i, j)$. The mean size of the step droplets $\langle n \rangle$ is then defined by

$$\langle n \rangle = \frac{1}{N_{\text{droplet}}} \sum_{i=1}^{N_i} \sum_{j=1}^{N_j} |n(i, j)|,$$

(26)

where $N_i = N_j = 240$ is the number of lattice units in the $i$ and $j$ directions, respectively. $N_{\text{droplet}}$ is calculated using $N_{\text{droplet}} = \sum_{j=1}^{N_j} N_{\text{droplet}}(j)$, where $N_{\text{droplet}}(j)$ represents the number of giant steps (step droplets) in the $j$th row of the square lattice shown in figure 18.

In figure 19(a), we plot $\langle n \rangle$ calculated using the Monte Carlo method against $p_r$, as expressed in equation (15). As
4. $p$-expanded expression for non-GMPT vicinal surface free energy

4.1. Breakdown of the homogeneous 1D fermion system

Let us consider the mean running direction of steps as the direction of time flow. If we consider a coarse-grained vicinal surface of the original RSOS model, the steps can be regarded as continuous lines describing the spacetime trajectories of Brownian particles with hard-core repulsion. If the particle density is low, the Hamiltonian for the transfer matrix in the continuous system is known to be described by 1D free fermions [21–23, 29], and the free energy is expressed by equation (1).

In the case of $\epsilon_{\text{int}} \neq 0$, since two fermions cannot be present at the same site at the same time, the transfer matrix for the $p$-RSOS model for a continuous system cannot be written as the Hamiltonian for interacting fermions. Using the transfer matrix of the RSOS model, which is similar to the p-RSOS model, den Nijs and Rommels mapped the RSOS model to a 1D quantum spin system [59]. Since the domain walls in the ordered phase correspond to the steps on the surface, the Hamiltonian for the transfer matrix in the continuous system is expressed in terms of interacting impenetrable bosons [88, 89].

In the case of $\epsilon_{\text{int}} < 0$, bound states such as molecules or clusters might be formed between bosons [90] depending on the strength of the attraction between the bosons. That is, $\gamma$ and $B$ in equation (1) can vary, depending on the properties of the bound state, such as the number of particles in a cluster. In contrast, in a 1D free fermion system, since $\gamma$ and $B$ are the microscopic quantities assigned to a fermion monomer in the continuous model, changes in these parameters are not allowed. In this way, the 1D fermion picture breaks down and we must take inhomogeneous effects such as cluster formation in the Bose gas into consideration (a similar argument is given in section 3.2).

4.2. Expression for non-GMPT vicinal surface free energy

We regard a giant step with a size $n$ as a boson-$n$-mer formed by microscopic step–step attraction $\epsilon_{\text{int}} < 0$. As time passes, these $n$-mers may grow or shrink in a similar manner to crystal clusters in the gas phase. Recalling the results described in section 3, we assume a system of 1D bosons made up of a mixture of different boson-$n$-mers as shown in figure 20. We refer to this inhomogeneous picture of a vicinal surface as the step-droplet picture.

Let us now consider such a many-body system of boson-$n$-mers (figure 20). We denote the density of giant steps with height $h$ by $n_h$. We assume that the interactions among $n$-mers are short range. The free energy $f_n(n_h)$ of a vicinal surface...
After some calculations (appendix B), we obtain

\[ f_d(\rho_n) = f(0) + \gamma_n(\phi) \rho_n + B_n(\rho) \rho_n^3 + C_n(\rho) \rho_n^4 + O(\rho_n^5), \]

(27)

where \( \gamma_n(\phi) \) represents the step tension of a giant step, \( B_n(\rho) \) represents the step interaction coefficient among giant steps, \( C_n(\rho) \) \((<0)\) represents the three-body interaction coefficient among giant steps\(^1\) and \( \phi \), similar to the case for a single step (figure 7), represents the angle between the mean running direction of the giant step and the y axis. In the limit \( \rho_n \to 0 \), \( \phi \) converges to \( \phi_0 \).

Recalling that \( \rho_n = N_{s,n}/L = |p|/d_n = |p|/(nd_n) \), where \( N_{s,n} \) is the total number of giant steps with size \( n \), \( L \) is the length of the projected area of the vicinal surface and \( d_n \) is the height of the giant steps, we obtain a \( |p| \)-expanded expression for \( f_n(\rho_n) \) as \( f_n(p) \) (appendix B, equation (B.1)). We then expand \( \gamma_n(\phi) \) and \( B_n(\rho) \) with respect to \( n \) around \( n = 1 \). After some calculations (appendix B), we obtain

\[ f_n(|p|) = f(0) + \left[ \left( \gamma_1(\phi) - \frac{\gamma_1(\phi)}{2} \right) + \frac{\gamma_1(\phi)}{2} \right] |p| \frac{d_1}{d_n} + \frac{B_1(\phi)}{d_n^4} |p|^3 d_1^3 \]

\[ + \left( \frac{1}{2} + \frac{1}{2} (n-1) \right) \frac{\gamma_1(\phi)}{\gamma_1(\phi)} + \frac{1}{2} (n-1) \frac{\gamma_2(\phi)}{\gamma_1(\phi)} \right]^{-1} \]

\[ \times \left[ \frac{C_n(\phi)}{n^4} |p|^4 \frac{d_1}{d_n^4} + O(|p|^5), \right. \]

(28)

where \( \gamma_1^{(m)}(\phi) \) and \( \gamma_2^{(m)}(\phi) \) are defined by

\[ \frac{\gamma_1^{(m)}(\phi)}{\gamma_1(\phi)} = \frac{\partial^m \gamma_n(\phi)/n}{\partial n}, \]

\[ \frac{\gamma_2^{(m)}(\phi)}{\gamma_1(\phi)} = \frac{\partial^m \gamma_n(\phi)/n}{\partial n}, \]

(29)

and \( \gamma_n(\phi) + \partial^2 \gamma_n(\phi)/\partial \phi^2 \) represents the stiffness of a giant step.

\(^1\) Note that \( C_0(\phi) \) \((<0)\) is caused by the RSOS restriction. The existence of the higher-order terms in the original RSOS system is confirmed numerically by figure 9(b).

Since \( n \) is difficult to estimate, we approximate equation (28) by replacing \( n \) with \( (n(\phi)) \). Recalling the results for \( (n(\phi)) \) obtained by the Monte Carlo calculations in section 3.3, we expand \( (n(\phi)) \) with respect to \( |p| \) around \( |p| = 0 \). Namely

\[ (n(\phi)) = 1 + n_0^{(1)}(\phi) |p| + \frac{1}{2} n_0^{(2)}(\phi) |p|^2 + \frac{1}{6} n_0^{(3)}(\phi) |p|^3 + \cdots, \]

(30)

Finally, substituting equation (30) into (28), and after some calculations, the non-GMPT vicinal surface free energy can finally be expressed as

\[ f_{\text{eff}}(p) = f(|p|) = f(0) + n_1(\phi) \frac{|p|}{d_1} + A_{\text{eff}}(\phi) |p|^2 \]

\[ + B_{\text{eff}}(\phi) |p|^3 + C_{\text{eff}}(\phi) |p|^4 + O(|p|^5), \]

(31)

where

\[ A_{\text{eff}}(\phi) = n_0^{(1)}(\phi) y_1^{(1)}(\phi)/d_1 \]

\[ B_{\text{eff}}(\phi) = \frac{1}{2 d_1} \left[ n_0^{(2)}(\phi) y_1^{(1)}(\phi) + n_0^{(1)}(\phi) y_1^{(2)}(\phi) \right] + \frac{B_1(\phi)}{d_1^2}, \]

(32)

\[ C_{\text{eff}}(\phi) = \frac{1}{6 d_1} \left[ n_0^{(3)}(\phi) y_1^{(1)}(\phi) + 3 n_0^{(2)}(\phi) n_0^{(2)}(\phi) y_1^{(2)}(\phi) \right] \]

\[ - B_1(\phi) n_0^{(1)}(\phi) \left[ \frac{1}{d_1^4} \left( 4 + \frac{y_1^{(1)}(\phi)}{y_1^{(1)}(\phi)} + \frac{C_n(\phi)}{n^4} \right) \right] \]

\[ = B_1(\phi) n_0^{(1)}(\phi) \left[ \frac{1}{d_1^4} \left( 4 + \frac{y_1^{(1)}(\phi)}{y_1^{(1)}(\phi)} + \frac{C_n(\phi)}{n^4} \right) \right]. \]

(34)

In equation (31), the term \( |p|^2 \) appears. In addition, \( B_{\text{eff}}(\phi) \) can be larger or smaller than \( B_1(\phi) \).

The microscopic quantities \( \epsilon \) and \( \epsilon_{\text{int}} \) do not appear explicitly in equation (31). They do, however, seem to determine mesoscopic quantities such as step tension, stiffness and mean height. The mean step height depends on the character of the step–step attraction (see figure 19(a)). In fact, the slope dependence of the mean step height for the RSOS-I model seems to be different to that for the p-RSOS model. A detailed study on the RSOS-I model will be reported elsewhere [91].

4.3. Thermodynamic expression for non-GMPT shape exponents

In order to derive the non-GMPT shape exponents thermodynamically, we write the \( |p| \)-expanded form of the vicinal surface free energy as

\[ f_\xi(p) = f(0) + \gamma(\phi) |p| + B_\xi(\phi) |p|^\xi + O(|p|^{\xi+1}), \]

(35)

where \( \xi > 1 \). We can then express the shape exponents thermodynamically as (appendix C)

\[ \theta_\ell = 2 \xi/(\xi - 1), \quad A_\ell(\phi) = \frac{1}{\theta_\ell} \left[ \frac{(k_B T)^{\xi+1}}{2 \xi B_\xi(\phi) \gamma(\phi)^\xi} \right]^{1/\xi}, \]

(36)
for the shape exponent along the tangential line ($\overline{QQ}$ in figure 7) and

$$\theta_n = \zeta / (\zeta - 1), \quad A_n(\phi) = \frac{1}{\theta_n} \left[ \frac{k_B T}{\zeta B_c(\phi)} \right]^{1/\gamma}.$$  \hspace{1cm} (37)

for the shape exponent along the normal line ($\overline{PP}$ in figure 7). From equations (36) and (37), we obtain the following relationships:

$$\theta_t = 2\theta_n,$$

$$r = \left[ \frac{A_0(\phi)}{A_n(\phi)} \right]^{1/\gamma} r^2 = \frac{k_B T}{2\gamma(\phi)} r^2.$$ \hspace{1cm} (39)

5. Application to the p-RSOS model

5.1. $T_{f,2} < T \leq T_{f,1}$

We compare the results of equations (36) and (37) for the non-GMPT free energy equation (31) with the numerical results in section 2 obtained by statistical mechanical calculations.

Figure 21 is a schematic diagram of the $r$-$p_r$ curve, where $C_{eff}(\phi)$ is assumed to be negative, $r$ is given by $r = \partial \xi_{eff}(\phi) / \partial p_r$, and $p_r$ is the surface slope along the line $\overline{PP}$ (figure 7). Let us define $p_r^{\pm}$ so that $\partial \xi(r) / \partial p_r = 0$. We then have

$$p_r^{\pm} = \frac{1}{12C_{eff}(\phi)} \times \left[ -3B_{eff}(\phi) \pm \sqrt{9B_{eff}(\phi)^2 - 24A_{eff}(\phi)C_{eff}(\phi)} \right].$$ \hspace{1cm} (40)

When $A_{eff}(\phi) > 0$ and $B_{eff}(\phi) < 0$, for $0 \leq p < p_1$, a vicinal surface with a regular train of steps is in an equilibrium state, for $p_1 < p < p_r^{+}$, it is metastable, and for $p_r^{+} < p < p_0$ ($p_0 = \sqrt{2}$), it is thermodynamically unstable.

For the temperature region $T_{f,2} < T \leq T_{f,1}$, we have $\gamma_1^{(1)}(\pi/4) > 0$ in section 2.3 and $\gamma_1^{(1)}(\pi/4) \geq 0$ in section 2.4, so that $A_{eff}(\pi/4) \geq 0$. From equations (36) and (37), we have

$$\theta_n = 2, \quad \theta_t = 4, \quad A_n = \frac{k_B T}{4A_{eff}(\pi/4)}.$$

By comparing equations (41) with the PWFRG results in section 2.4, we see that the non-universal shape exponents for the p-RSOS model agree with the values obtained using equations (41). Moreover, by comparing the amplitudes of equations (41) with the PWFRG results in section 2.4, we obtain $\beta A_{eff}(\pi/4) = (6.22 \pm 0.06) \times 10^{-3}$ and $\beta \gamma_1(\pi/4) = 1.39 \pm 0.03$. This value of $\beta \gamma_1(\pi/4)$ agrees well with $\beta \tilde{\gamma}_1(\pi/4)$ from equation (18). Consequently, in the $p_r \to 0$ limit, step droplets ‘evaporate’ and dissociate into individual steps with $n = 1$. Substituting the value of $\beta A_{eff}(\pi/4)$ and the value of $\gamma_0^{(1)}(\pi/4) = 2.26$ obtained from figure 19 into equation (32), we have $\beta \gamma_1^{(1)}(\pi/4) = (2.75 \pm 0.05) \times 10^{-3}$. The small value of $\beta \gamma_1^{(1)}(\pi/4)$ is consistent with experimental observations on Si(113) [92].

5.2. $T > T_{f,1}$

From the results in section 2.4, a vicinal surface with small $p_r$ shows the GMPT universal behavior of single steps. Near $p_r \approx 0$, therefore, $A_{eff}(\pi/4) = 0$, and then $\gamma_1^{(1)}(\pi/4)$ is considered to be zero. Hence, we have from equations (37), (36) and (31):

$$\theta_n = 3/2, \quad \theta_t = 2\theta_n = 3,$$

$$p_x = p_r / \sqrt{2} = \left[ \frac{k_B T}{6B_{eff}(\pi/4)} \right]^{1/2},$$

$$|p_x - p_y| = \sqrt{2} p_l = \left[ \frac{k_B T}{\sqrt{3B_{eff}(\pi/4)\tilde{\gamma}_1(\pi/4)^3}} \right] |t|.$$ \hspace{1cm} (43)

By comparing equations (43) with the curve calculated using the PWFRG method, we have $\beta B_{eff}(\pi/4) = 0.281 \pm 0.008$. $\beta B_{eff}(\pi/4)$ at $k_B T / \epsilon = 0.37$ is estimated as $\beta B_{eff}(\pi/4) = 1.206$ by use of the step stiffness of the Ising model (equation (18)).

Then, from equation (33) with $\nu_0^{(1)} = 1.45$ (figure 19) and with $\gamma_1^{(1)}(\pi/4) = 0$, we have $\beta \gamma_1^{(2)}(\pi/4) = -0.88 \pm 0.08$.

5.3. $T \leq T_{f,2}$

In the low temperature region, the first-order shape transition occurs at the (001) facet edge on the ECS profile. If we consider $A_{eff}(\pi/4) < 0$ and $B_{eff}(\pi/4) < 0$ (figure 21), the first-order shape transition can be understood in terms of the non-GMPT vicinal surface free energy $\xi_{eff}(\phi)$ (equation (31)). From the EFS results (section 2.3), we have $\gamma_1^{(1)}(\pi/4) < 0$, and from the Monte Carlo calculation of $\langle n \rangle$ at $k_B T / \epsilon = 0.35$ we have $\gamma_0^{(1)} > 0$. These results are consistent with $A_{eff}(\pi/4) < 0$.

6. Summary and discussion

In section 2, we present statistical mechanical calculations on the vicinal surface of the restricted solid-on-solid (RSOS)
model with a point-contact-type step–step attraction (p-RSOS model) (figure 2). Applying the product wavefunction renormalization group (PWFRG) method, which is a variant of the density matrix renormalization group (DMRG) method, to the transfer matrix for the p-RSOS model, we calculate the reduced equilibrium crystal shape (ECS) of the p-RSOS model (figure 6) and the surface gradient $p = (p_x, p_y)$ as a function of $X = (\beta \eta_x = -\beta \lambda x, \beta = 1/k_B T)$ and $Y = (\beta \eta_y = -\beta \lambda y)$ (figure 9).

We obtain the first-order shape transition around the (111) facet on the ECS profile for $T < T_{f,1}$. For $T < T_{f,2}$, a first-order shape transition at the (001) facet edge is also observed on the ECS profile, where the (001) facet directly contacts the (111) facet (figure 10). By analyzing the PWFRG results, we obtain the equilibrium facet shape (figure 10) and the step tension; for the vicinal surface tilted towards the (110) direction, we obtain the step stiffness, the non-GMPT shape exponents (figure 11) and the non-GMPT amplitudes (figure 12).

In section 3, in order to elucidate the origin of the non-GMPT behavior, we study step droplets formed by thermal step bunching on the vicinal surface tilted towards the (110) direction for the p-RSOS model. We calculate the vicinal surface free energy from the Andreev surface free energy obtained from the PWFRG calculations (figure 14).

Step bunching near equilibrium caused by a singularity in the surface free energy (figure 15) is demonstrated using Monte Carlo simulations with a simple Metropolis algorithm (figures 16 and 17). To obtain a clear image of local step droplets, we demonstrate giant step formation similar to step faceting for $T \leq T_{f,2}$. From a microscopic point of view, these giant steps are formed from sticky steps due to the step–step attraction. For $T_{f,2} \leq T \lesssim T_{f,1}$, the giant steps partially dissociate due to entropic repulsion. Using a long-duration Monte Carlo simulation, we calculate the slope dependence of the mean step number $\langle n \rangle$ in a giant step (figure 19) and find that $\langle n \rangle$ increases linearly with $|p|$.

In section 4, we derive a $|p|$-expanded form of the non-GMPT vicinal surface free energy $f_{\text{eff}}(p)$ (equation (31)). In equation (31), $|p|^2$ term appears. In the derivation, the concept of step droplets (boson $n$-mers, figure 20) and knowledge of the slope dependence of $\langle n \rangle$ obtained in the long-duration Monte Carlo calculation in section 3.3 are crucial.

In section 5, the results in section 2 are consistently reproduced by thermodynamical calculations based on the non-GMPT vicinal surface free energy $f_{\text{eff}}(p)$. By comparing the results in section 2 with the results obtained using $f_{\text{eff}}(p)$, we obtain information on the derivative of $n_\gamma, \partial(n_\gamma/n)_{\beta l}$. Whereas it is negative for $T < T_{f,2}$ and zero for $T > T_{f,1}$, $\partial^2(n_\gamma/n)/\partial n_{\beta l}^2 < 0$ for $T \approx T_{f,1}$ and the step droplets are dispersed in the limit $|p| \rightarrow 0$.

The first-order transition on the ECS profile has been studied theoretically by several authors [26, 27]. Rottman and Wortis [26] calculated the interface tension using a 3D cubic Ising model with both nn and next-nearest-neighbor (nnn) interactions between spins by means of the mean-field approximation. They found the first-order shape transition around the (001) facet at low temperature for the negative nnn interactions. However, they did not discuss the shape exponent for the temperature range $T_3 < T < T_1$ (using their terminology). Jayaprakash et al [27] studied the vicinal surface of the interacting terrace-step-kink (TSK) model with long-range step–step attractions corresponding to attractive dipolar interactions. They determined the surface free energy using mean-field calculations and showed that the surface free energy $f(p)$ has the form of the GMPT (equation (1)) and that the long-range attractions change $B$. When $B$ becomes negative, the facet edge causes the first-order shape transition. This explanation for the first-order shape transition is limited to the case of attractive long-range step–step interactions, because in the case of short-range attractions $B$ does not change. Hence, the explanation based on step droplets described in section 4.2 is required.

In real systems, there are a variety of different surface effects that occur, as described in section 3.3.1. Of these, elastic interactions among steps are the most important source of long-range step–step repulsion. The TSK model with a long-range step–step repulsion of the order of $\sim 1/l^2$, where $l$ is the inter-step distance, is known to have the GMPT universal free energy [27, 31] in a homogeneous system, and the system has the GMPT universal shape exponents on the ECS. The work of Shenoj et al [81] suggests that step bunching occurs as $m$-mers of particles in the TSK model with a long-range step–step repulsion of the order of $\sim 1/l^2$ and a short-range step–step attraction. In this case, if $m$ depends on $p$, then the non-GMPT shape exponents on the ECS are expected from equations (31)–(34).

Paulin et al [93, 95] considered a surface system with an elastic interaction of $\sim 1/l^2 \ln l$ in order to study the dynamical behavior of the single-step to double-step transition on the Si(001) surface. Such an elastic interaction is thought to change the absolute values of the step tension, stiffness and interaction coefficient (using our terminology), as in the case of $\sim 1/l^2$ [31]. As long as a homogeneous system is realized (‘in-phase meandering’ using their terminology), an elastic interaction of $\sim 1/l^2 \ln l$ probably does not change the shape exponents. However, in the case of ‘out-of-phase meandering’, since inhomogeneity is suggested, non-GMPT shape exponents are expected due to the step droplets as explained in section 4.2.

Recently, a first-order-like shape change for $^4$He around the (0001) facet has been reported [94]. The strong anisotropy in the surface stiffness measured in the experiment suggests the existence of a singularity in the surface free energy. The results of the present study and those in our previous reports [54, 55] are consistent with this finding.

7. Conclusion

In the present study, we investigate a vicinal surface tilted towards the (110) direction near a (001) facet on the ECS of the p-RSOS model. For $T_{f,2} < T \lesssim T_{f,1}$, the shape exponents on the ECS have non-GMPT values such as $\theta_h = 2$ for the normal direction and $\theta_t = 4$ for the tangential
direction. The origin of the non-GMPT shape exponents is the formation of step droplets ('giant steps') with different sizes. The non-GMPT expression for the vicinal surface free energy \( f_{\text{eff}}(p) \) is derived. In the derivation, knowledge of the \(|p|\) dependence of the mean step-droplet size is crucial. The results obtained by statistical mechanical calculations using the p-RSOS model are successfully reproduced using thermodynamical calculations based on \( f_{\text{eff}}(p) \).

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**Appendix A. Exact expressions for interface tension and interface stiffness on a two-dimensional square Ising model**

The exact expression for the 2D ECS for an nn square Ising model [68–71] is written using the angle \( \phi \) in figure 7(b) as follows:

\[
\frac{\partial D(X, Y)}{\partial Y} \bigg|_{(X,Y)=(X_c,Y_c)} = \tan \phi \left[ \frac{\partial D(X, Y)}{\partial X} \bigg|_{(X,Y)=(X_c,Y_c)} \right] = 0, (A.1)
\]

where \( D(X, Y) \) is

\[
D(X, Y) = \cosh(X) + \cosh(Y) - \frac{\cos^2(\beta \epsilon)}{\sin(\beta \epsilon)}.
\]

Hence, the equation for the ECS on the 2D square nn Ising model becomes

\[
\cosh(X_c) + \cosh(Y_c) = \frac{\cos^2(\beta \epsilon)}{\sin(\beta \epsilon)}.
\]

Let us denote the anisotropic interface (step) tension for an interface with a mean running direction parallel to the line \( \overrightarrow{OD} \) by \( \gamma(\phi) \) (figure 7), and let us consider the interface stiffness \( \tilde{\gamma}(\phi) = \gamma(\phi) + \partial^2 \gamma(\phi)/\partial \phi^2 \). The exact expression for the interface stiffness for the 2D nn Ising model is derived by use of \( D(X, Y) \) (equation (A.1)) with equation (13), \( \partial^2 D(X(x), Y(\phi))/\partial \phi^2 \big|_{(X,Y)=(X_c,Y_c)} = 0 \) and \( \partial^2 D(X(x), Y(\phi))/\partial \phi^2 \big|_{(X,Y)=(X_c,Y_c)} = 0 \) as follows:

\[
\beta \tilde{\gamma}(\phi)_{\text{Ising}} = \left[ \frac{\partial D(X, Y)}{\partial X} \cos \phi + \frac{\partial D(X, Y)}{\partial Y} \sin \phi \right] \times \left[ \frac{\partial^2 D(X, Y)}{\partial X^2} \sin^2 \phi + \frac{\partial^2 D(X, Y)}{\partial Y^2} \cos^2 \phi \right] - \frac{2 \partial^2 D(X, Y)}{\partial Y \partial X} \sin \phi \cos \phi \bigg|_{(X,Y)=(X_c,Y_c)}.
\]

**Appendix B. Derivation of the non-GMPT vicinal surface free energy**

We investigate the \( n \) dependence of \( f_n(\rho_n) \) for \( \rho_n \approx 0 \). \( \rho_n \) is expressed as \( \rho_n = N_{n,s}/L = |p|/d_n \), where \( N_{n,s} \) is the total number of giant steps with size \( n \), \( L \) is the length of the projected area of the vicinal surface and \( d_n \) is the height of the giant step. \( L \) is assumed to be sufficiently large so that we may take the thermodynamic limit. Substituting the expressions for \( \rho_n \) and \( d_n \) into equation (27), we have

\[
f_n(p) = f(0) + \frac{\gamma_n(\phi)}{d} |p| + \frac{B_n(\phi)}{d^3 n^3} |p|^3 + \frac{C_n(\phi)}{d^4 n^4} |p|^4 + O(p^5).
\]

(B.1)

Since \( \gamma_n(\phi) \) is considered to be approximately equal to \( n \gamma_1(\phi) \) with respect to \( n \) around \( n = 1 \) as follows:

\[
\gamma_n(\phi)/n = \gamma_1(\phi) + \frac{1}{2} \gamma_1(\phi)(n-1)^2 + \cdots.
\]

(B.2)

Assuming the universal relation, equation (17), where \( \tilde{\gamma}_n(\phi) \) represents the stiffness of the giant step \( \tilde{\gamma}_n(\phi) = \gamma_n(\phi) + \partial^2 \gamma_n(\phi)/\partial \phi^2 \), we expand \( \tilde{\gamma}_n(\phi) \) instead of \( B_n(\phi) \). That is

\[
\tilde{\gamma}(\phi)/n = \tilde{\gamma}_1(\phi) + \frac{1}{2} \tilde{\gamma}_1(\phi)(n-1)^2 + \cdots.
\]

(B.3)

Substituting equations (B.2) and (B.3) into equation (B.1), we have equation (28).

**Appendix C. Thermodynamic derivation of the shape exponents**

Equations (36)–(39) are derived from the extended vicinal surface free energy \( f_s(p) \) (equation (35)). In the following manner, we consider the case where the first-order shape transition does not occur on the contour of the (001) facet.

From the thermodynamics of the ECS [8], the coordinates \((X, Y)\) on the reduced ECS are obtained from \( f(p) \) as follows [28]:

\[
X = \beta \frac{\partial f(p)}{\partial p_x}, \quad Y = \beta \frac{\partial f(p)}{\partial p_y},
\]

(C.1)

where \( \beta = 1/k_BT \). Then the reduced coordinates \((X, Y)\) on the ECS are written as

\[
X = X_c(\phi) + |p| \zeta^{-1} [\beta \zeta B_c(\phi) \cos \phi - \beta B'_c(\phi) \sin \phi],
\]

\[
Y = Y_c(\phi) + |p| \zeta^{-1} [\beta \zeta B_c(\phi) \sin \phi + \beta B'_c(\phi) \cos \phi],
\]

\[
B'_c(\phi) = \partial B_c(\phi)/\partial \phi,
\]

(C.2)
Combining (C.4) with (C.2) and equation (C.3), we obtain

\[ \Theta \] with respect to \( \phi \).

Similarly, along the normal line (equation (C.6)), we obtain expressions for the tangential shape exponent \( \theta_n \) as follows:

\[ \Delta X = \left( \frac{A_n(0)}{\tilde{A}_n(0)} \right) \frac{1}{\tilde{\gamma}(0)} \Delta Y^2 = \frac{k_B T}{2 \tilde{\gamma}(0)} \Delta Y^2. \] (C.10)

This expression is also obtained geometrically from figure C.1(b) using the radius of curvature \( R \) such that \( \Delta X = \Delta Y^2/(2R) = k_B T \Delta Y^2/(2 \tilde{\gamma}(0)) \) [66] and \( \Delta X = \Delta X \) for small \( \Delta X \) and \( \Delta Y \).

\[ \Theta \]

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\[ \Theta \]
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