Determining absolute orientation-dependent step energies: a general theory for the Wulff-construction and for anisotropic two-dimensional island shape fluctuations

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Abstract

We describe an analytical form of the Wulff plot construction procedure and derive a general expression for the surface energy from the three-dimensional equilibrium crystal shape in generalized orthogonal curvilinear coordinates. Particular expressions in Cartesian, spherical polar, and circular cylindrical coordinates are also presented. Corresponding results for a two-dimensional (2D) island on a flat terrace provide relative orientation-dependent step energies within a scale factor λ, the equilibrium chemical potential of the island per unit area. In order to determine λ and, hence obtain absolute step energies, we have developed an exact theoretical approach, applicable to both isotropic and anisotropic 2D island shapes, relating the temporal change in island free energy to thermal fluctuations about the equilibrium shape.
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1. Introduction

The surface free energy per unit area γ is a fundamental parameter used to describe crystals. The variation of γ with surface orientation determines the three-dimensional (3D) equilibrium crystal shape (ECS). The two-dimensional (2D) analog of γ is the step formation energy per unit length β. Just as $\gamma(\hat{\mathbf{n}})$, where $\hat{\mathbf{n}}$ is a unit vector

normal representing a surface orientation, determines the equilibrium shape of 3D crystals, $\beta(\varphi)$, where φ is the step orientation, determines the equilibrium shape of 2D islands on a terrace. Given the fundamental importance of $\gamma(\hat{\mathbf{n}})$ and $\beta(\varphi)$, it is surprising how little information is available concerning these parameters even for simple elemental metal surfaces.

The well-known Wulff construction provides a method to determine the 3D ECS from the "Wulff plot", a polar representation of $\gamma(\hat{\mathbf{n}})$ [1]. Geometrically, the procedure involves drawing planes perpendicular to the normal unit vectors at every point on the surface free energy $\gamma(\hat{\mathbf{n}})$. The inner

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envelope of these planes then corresponds to the ECS. Similarly, the "inverse" Wulff construction determines $\gamma(\hat{\mathbf{n}})$ from the ECS by drawing normal vectors to the tangent planes along the crystal boundary. The envelope of these vectors yields *relative* values of $\gamma(\hat{\mathbf{n}})$. Mathematically, the equilibrium shape function is the Legendre transform of $\gamma(\hat{\mathbf{n}})$ and vice versa. Analytical expressions for the Wulff construction have been derived generally and in Cartesian coordinates [1–3]. For 2D islands, Nozières [3] derived an expression in polar coordinates relating β to the equilibrium shape.

With the advent of surface imaging techniques, such as low-energy electron microscopy (LEEM) and scanning tunneling microscopy (STM), 2D islands on flat terraces and facets on 3D ECSs can be routinely observed as a function of temperature, thus providing experimental tools for determining the relative orientation dependence of β. However, experimental determinations of *absolute* $\gamma(\hat{\mathbf{n}})$ and/or $\beta(\varphi)$ values are difficult.

Bombis et al. [4] used a combination of 3D ECS and step energy measurements to extract absolute values of γ. Absolute β values for *fixed* orientations have been determined from step stiffnesses $\tilde{\beta}$ obtained from step fluctuation measurements [5], from 3D ECSs [6], and from the temperature-dependence of 2D equilibrium island shapes [7,8]. Orientation-averaged β values have been extracted from 2D island decay measurements [9–11] and from near-isotropic island shape fluctuation measurements [12]. Newer methods, based upon 2D equilibrium shape and either island decay or temporal island shape-fluctuation measurements for determining absolute orientation-dependent step energies and step stiffnesses, are implemented in Refs. [13,14]. A novel asymmetric Wulff plot construction to describe island shapes observed on the Au(1 1 0) surface has also been reported recently [15].

In this article, we present a detailed theoretical formalism for extracting absolute $\beta(\varphi)$ values from an analysis of temporal fluctuations about *any* arbitrary shape of 2D equilibrium islands at one temperature. The results are organized as follows. Analytical expressions relating surface and step energies to 3D ECS and 2D single layer adatom or vacancy equilibrium shapes, respec-

tively, are derived in a generalized orthogonal curvilinear coordinate system in Section 2. Relations for $\beta(\varphi)$ in terms of the 2D equilibrium island shape are presented in Section 3. These results provide relative $\beta(\varphi)$ values within an orientation-independent scale factor λ, the equilibrium island chemical potential per unit atomic area. An *exact* expression relating the temporal change in island free energy, a function of λ, to thermal fluctuations about the equilibrium shape is derived in Section 4. In contrast to earlier analyses [12,16], our approach requires no assumptions regarding island isotropy.

2. Wulff construction in generalized coordinates

Here we derive an analytical expression relating the surface energy to the 3D ECS in generalized orthogonal coordinates using a Legendre transformation procedure. We also derive the inverse transform relations to determine the 3D equilibrium shape from the surface energy $\gamma(\hat{\mathbf{n}})$. The equations can easily be generalized to *N*-dimensions by modifying the constant *c* in Eqs. (10a) and (10b).

Consider an infinitely large 3D crystal whose surface is described by the equation

$$W(x_1, x_2, x_3) = 0 \qquad (1)$$

in generalized orthogonal coordinates x_1, x_2, and x_3 such that the origin O of the coordinate system coincides with the center of mass of the crystal. We define $W(x_1, x_2, x_3)$ in terms of the equilibrium shape function S as

$$W(x_1, x_2, x_3) \equiv (\vec{\mathbf{R}} \cdot \hat{\mathbf{e}}_3) - S(x_1, x_2), \qquad (2)$$

where $\vec{\mathbf{R}}$ is the position vector of point (x_1, x_2, x_3) with respect to O and $\hat{\mathbf{e}}$ ($i = 1$, 2, and 3) are unit vectors along the coordinate axes x_1, x_2, and x_3, respectively. The equilibrium shape function $S(x_1, x_2)$ specifies the precise form of the ECS. Fig. 1 is a geometric representation of the inverse Wulff construction procedure for an arbitrary equilibrium shape $W(x_1, x_2, x_3) = 0$. The local unit normal $\hat{\mathbf{n}}$ to the ECS is given by

$$\hat{\mathbf{n}}(s_1, s_2) = \frac{\vec{\nabla} W(s_1, s_2)}{|\vec{\nabla} W(s_1, s_2)|}, \qquad (3)$$
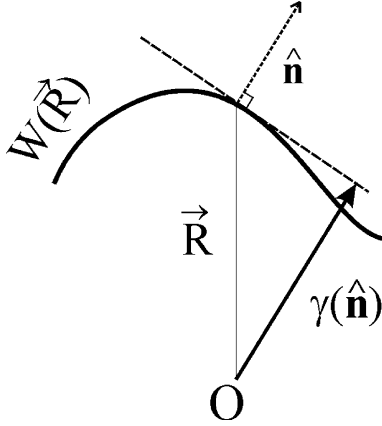
Fig. 1. Geometrical representation of the inverse Wulff plot construction: at each point $\vec{\mathbf{R}} = (x_1, x_2, x_3)$ on the equilibrium crystal shape defined by $W(x_1, x_2, x_3) = 0$, a plane is drawn tangential to the surface. The distance of the plane from the origin O is proportional to $\gamma(\hat{\mathbf{n}})$, where $\hat{\mathbf{n}}$ is the unit normal vector to the plane.

where the gradient $\vec{\nabla}(s_1, s_2)$ to the surface can be expressed as [17]

$$\vec{\nabla} W(s_1, s_2) = \sum_{i=1}^{3} \left(\frac{\hat{\mathbf{e}}_i}{h_i} \right) \frac{\partial W}{\partial x_i}$$
$$= \frac{\hat{\mathbf{e}}_3}{h_3} - \frac{s_1 \hat{\mathbf{e}}_1}{h_1} - \frac{s_2 \hat{\mathbf{e}}_2}{h_2} \tag{4}$$

with

$$s_i \equiv \frac{\partial S(x_1, x_2)}{\partial x_i} \quad \text{(for } i = 1 \text{ and 2).} \tag{5}$$

The new coordinates s_i ($i = 1, 2$) are the slopes of the equilibrium shape function $S(x_1, x_2)$ along the coordinate directions. Note that $\hat{\mathbf{n}}$ and $\vec{\nabla} W$ are functions of only two variables, though W is a function of three variables. The scale factors h_j ($j = 1, 2,$ and 3) in Eq. (4) are related to the in-finitesimal displacement vector $\mathbf{d}\vec{\mathbf{r}}$ expressed in generalized coordinates as [17]

$$\mathbf{d}\vec{\mathbf{r}} = \sum_{i=1}^{3} (h_i \, \mathrm{d}x_i) \hat{\mathbf{e}}_i. \tag{6}$$

Thermodynamically, a 3D ECS is defined as the surface with the minimum free energy for a fixed volume [1–3]. Thus, we construct a free energy functional F, accounting for the constant volume with a Lagrange multiplier Λ, as

$$F = \int_{W=0} \gamma(\hat{\mathbf{n}}) \, \mathrm{d}A - \Lambda \int_V \mathrm{d}V, \tag{7}$$

where V is the volume enclosed by the surface, $\mathrm{d}V = (\vec{\mathbf{R}} \cdot \hat{\mathbf{e}}_3) h_1 h_2 h_3 \, \mathrm{d}x_1 \, \mathrm{d}x_2$ is an infinitesimal strip of volume enclosed under an infinitesimal area $\mathrm{d}A$ of the surface and the $x_1 - x_2$ coordinate sheet. γ is a function of the local surface orientation $\hat{\mathbf{n}}$ only and Λ is the equilibrium chemical potential of the crystal per unit volume. The area element $\mathrm{d}A$ can be expressed using Eqs. (3) and (4), in terms of its projection onto the $x_1 - x_2$ sheet as

$$\mathrm{d}A = \frac{h_1 h_2 \, \mathrm{d}x_1 \, \mathrm{d}x_2}{\hat{\mathbf{n}} \cdot \hat{\mathbf{e}}_3} = |\vec{\nabla} W| (h_1 h_2 h_3 \, \mathrm{d}x_1 \, \mathrm{d}x_2). \tag{8}$$

Substituting Eq. (8) into Eq. (7) and applying the minimization condition $(\delta F / \delta(\vec{\mathbf{R}} \cdot \hat{\mathbf{e}}_3)) = 0$, we obtain

$$\Lambda = \left[\frac{\partial}{\partial(\vec{\mathbf{R}} \cdot \hat{\mathbf{e}}_3)} - \frac{\mathrm{d}}{\mathrm{d}x_1} \left(\frac{\partial}{\partial s_1} \right) \right.$$
$$\left. - \frac{\mathrm{d}}{\mathrm{d}x_2} \left(\frac{\partial}{\partial s_2} \right) \right] [\gamma(\hat{\mathbf{n}}) |\vec{\nabla} W|]. \tag{9}$$

The solution to Eq. (9) is

$$\gamma(\hat{\mathbf{n}}) = \frac{(\Lambda d)}{c}, \tag{10a}$$

where d is the distance from the origin to the plane tangential to the surface at $\vec{\mathbf{R}}$ and is given by the relation

$$d \equiv \vec{\mathbf{R}} \cdot \hat{\mathbf{n}}(s_1, s_2)$$
$$= \frac{1}{|\vec{\nabla} W|} \left(\frac{S(x_1, x_2)}{h_3} - \frac{s_1(\vec{\mathbf{R}} \cdot \hat{\mathbf{e}}_1)}{h_1} - \frac{s_2(\vec{\mathbf{R}} \cdot \hat{\mathbf{e}}_2)}{h_2} \right). \tag{10b}$$

For the 3D case considered here, the proportionality constant c in Eqs. (10a) and (10b) is 2. (In general, $c = (N - 1)$ for a surface in N-dimensional space.) Thus, Eqs. (10a) and (10b), the analytical expression of Wulff's theorem, can be used together with Eq. (3) to determine facet energies for any arbitrary ECS in any coordinate system.

Conversely, if the function $\gamma(\hat{\mathbf{n}})$ is known, then the ECS can be easily obtained. Partial differentiation of Eqs. (10a) and (10b) with respect to s_i (for $i = 1, 2$) results in the relation

$$\vec{\mathbf{R}} \cdot \hat{\mathbf{e}}_i = -\left(\frac{h_i c}{\Lambda}\right) \frac{\partial(\gamma(\hat{\mathbf{n}})|\vec{\nabla}W|)}{\partial s_i}. \tag{11}$$

Upon rearranging terms in Eqs. (10a) and (10b), we obtain the solution for $\vec{\mathbf{R}} \cdot \hat{\mathbf{e}}_3 = S(x_1, x_2)$ as

$$S(x_1, x_2) = h_3 \left[\frac{c\gamma(\hat{\mathbf{n}})|\vec{\nabla}W|}{\Lambda} + \frac{s_1(\vec{\mathbf{R}} \cdot \hat{\mathbf{e}}_1)}{h_1} + \frac{s_2(\vec{\mathbf{R}} \cdot \hat{\mathbf{e}}_2)}{h_2} \right]. \tag{12}$$

Thus, we recover the shape function $S(x_1, x_2)$ from $\gamma(\hat{\mathbf{n}})$. We note that Eq. (12) alone is not sufficient to describe completely the inverse Wulff construction. Only together with Eq. (11) is it possible to perform the inverse Legendre transform in Eq. (12). Thus, Eq. (11) is the inversion analog to Eq. (3). An example of the inverse transformation of Eqs. (11) and (12) will be explicitly performed in the 2D case; see Eqs. (19a) and (19b).

Eqs. (10a), (10b) and (12) represent analytical expressions of the Wulff theorem in generalized orthogonal coordinates. Equilibrium shapes for most crystalline materials can be conveniently described in Cartesian, spherical polar, or cylindrical coordinates. Therefore, we now derive surface energy relations for these three cases.

In Cartesian coordinates, $x_1 = x$, $x_2 = y$, $x_3 = z(x, y)$ and $\hat{\mathbf{e}}_1 = \hat{\mathbf{i}}$, $\hat{\mathbf{e}}_2 = \hat{\mathbf{j}}$, $\hat{\mathbf{e}}_3 = \hat{\mathbf{k}}$; and the scale factors h_j, defined in Eq. (6), are all equal to unity. Thus, Eqs. (10a), (10b) and (3) become

$$\gamma(\hat{\mathbf{n}}) = \left(\frac{\Lambda}{2}\right) \frac{(z - x\left(\frac{\partial z}{\partial x}\right) - y\left(\frac{\partial z}{\partial y}\right))}{[1 + \left(\frac{\partial z}{\partial x}\right)^2 + \left(\frac{\partial z}{\partial y}\right)^2]^{1/2}} \tag{13a}$$

and

$$\hat{\mathbf{n}} = \frac{\hat{\mathbf{k}} - \hat{\mathbf{i}}\left(\frac{\partial z}{\partial x}\right) - \hat{\mathbf{j}}\left(\frac{\partial z}{\partial y}\right)}{[1 + \left(\frac{\partial z}{\partial x}\right)^2 + \left(\frac{\partial z}{\partial y}\right)^2]^{1/2}}, \tag{13b}$$

respectively.

In cylindrical coordinates, we choose $x_1 = R$, $x_2 = \theta$, and $x_3 = z(R, \theta)$ to represent the radial, azimuthal, and height coordinates, respectively. This yields $h_1 = 1$, $h_2 = R$, and $h_3 = 1$.

Substituting into Eqs. (10a) and (10b), we obtain an expression for $\gamma(\hat{\mathbf{n}})$ in terms of the equilibrium shape $z(R, \theta)$ as

$$\gamma(\hat{\mathbf{n}}) = \left(\frac{\Lambda}{2}\right) \frac{\left(z - R\left(\frac{\partial z}{\partial R}\right)\right)}{\left[1 + \left(\frac{\partial z}{\partial R}\right)^2 + \frac{1}{R^2}\left(\frac{\partial z}{\partial \theta}\right)^2\right]^{1/2}} \tag{14a}$$

with

$$\hat{\mathbf{n}} = \frac{\hat{\mathbf{z}} - \hat{\mathbf{R}}\left(\frac{\partial z}{\partial R}\right) - \frac{\hat{\boldsymbol{\theta}}}{R}\left(\frac{\partial z}{\partial \theta}\right)}{\left[1 + \left(\frac{\partial z}{\partial R}\right)^2 + \frac{1}{R^2}\left(\frac{\partial z}{\partial \theta}\right)^2\right]^{1/2}}, \tag{14b}$$

where

$$\hat{\mathbf{R}} \equiv \begin{bmatrix} \cos\theta \\ \sin\theta \\ 0 \end{bmatrix}, \quad \hat{\boldsymbol{\theta}} \equiv \begin{bmatrix} -\sin\theta \\ \cos\theta \\ 0 \end{bmatrix}, \quad \text{and} \quad \hat{\mathbf{z}} \equiv \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

are the unit vectors expressed in Cartesian coordinates.

In spherical coordinates, we choose $x_1 = \theta$, $x_2 = \varphi$, and $x_3 = R(\theta, \varphi)$ as the polar, azimuthal, and radial coordinates, respectively, with $h_1 = R$, $h_2 = R\sin\theta$, and $h_3 = 1$. After substitution into Eqs. (10a) and (10b), we obtain

$$\gamma(\hat{\mathbf{n}}) = \left(\frac{\Lambda}{2}\right) \left[\frac{R}{\left[1 + \frac{1}{R^2}\left(\frac{\partial R}{\partial \theta}\right) + \frac{1}{R^2\sin^2\theta}\left(\frac{\partial R}{\partial \varphi}\right)^2\right]^{1/2}} \right] \tag{15a}$$

with

$$\hat{\mathbf{n}} = \frac{\hat{\mathbf{R}} - \frac{\hat{\boldsymbol{\theta}}}{R}\left(\frac{\partial R}{\partial \theta}\right) - \frac{\hat{\boldsymbol{\varphi}}}{R\sin\theta}\left(\frac{\partial R}{\partial \varphi}\right)}{\left[1 + \frac{1}{R^2}\left(\frac{\partial R}{\partial \theta}\right)^2 + \frac{1}{R^2\sin^2\theta}\left(\frac{\partial R}{\partial \varphi}\right)^2\right]^{1/2}}, \tag{15b}$$

where

$$\hat{\mathbf{R}} \equiv \begin{bmatrix} \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \\ \cos\theta \end{bmatrix}, \quad \hat{\boldsymbol{\varphi}} \equiv \begin{bmatrix} -\sin\varphi \\ \cos\varphi \\ 0 \end{bmatrix}, \quad \text{and}$$

$$\hat{\boldsymbol{\theta}} \equiv \begin{bmatrix} \cos\theta\cos\varphi \\ \cos\theta\sin\varphi \\ -\sin\theta \end{bmatrix}$$

are the unit vectors.

3. 2D Wulff construction in polar coordinates

The above results for the 3D ECS can easily be reduced to describe 2D equilibrium shapes by ignoring all terms in the coordinate x_2 and replacing the 3D functions γ and Λ with their 2D analogs β (the step energy per unit length) and λ (the chemical potential per unit surface area). In the following discussion, a symbol with a dot over it signifies its derivative with respect to θ. In polar coordinates, we obtain

$$\beta(\hat{\mathbf{n}}) = \lambda \frac{R(\theta)}{\left[1 + \left(\frac{\dot{R}(\theta)}{R(\theta)}\right)^2\right]^{1/2}} \tag{16a}$$

and

$$\hat{\mathbf{n}} = \frac{\hat{\mathbf{R}} - \hat{\boldsymbol{\theta}}\left(\frac{\dot{R}(\theta)}{R(\theta)}\right)}{\left[1 + \left(\frac{\dot{R}(\theta)}{R(\theta)}\right)^2\right]^{1/2}} \tag{16b}$$

for which

$$\hat{\mathbf{R}} = \begin{bmatrix} \cos\theta \\ \sin\theta \end{bmatrix} \quad \text{and} \quad \hat{\boldsymbol{\theta}} = \begin{bmatrix} -\sin\theta \\ \cos\theta \end{bmatrix}$$

are the unit vectors. The step orientation is given by φ, defined as the angle between the local normal to the equilibrium shape at R and the x-axis. Thus, substituting for the unit vectors $\hat{\mathbf{R}}$ and $\hat{\boldsymbol{\theta}}$ in Eq. (16b) yields the relation

$$\varphi \equiv \arctan\left(\frac{\hat{\mathbf{n}} \cdot \hat{\mathbf{j}}}{\hat{\mathbf{n}} \cdot \hat{\mathbf{i}}}\right)$$
$$= \theta - \arctan[\dot{R}(\theta)/R(\theta)] \tag{17a}$$

and

$$\beta(\varphi) = \lambda \frac{R^2(\theta)}{\sqrt{R^2(\theta) + (\dot{R}(\theta))^2}}. \tag{17b}$$

We observe that Eq. (17b), with λ set to unity, is equivalent to the relation $\beta(\varphi) = R\cos(\varphi - \theta)$ derived by Nozières [3].

It is important to note that the equation $\beta_1/\beta_2 = R_1/R_2$, often referred to as the "Wulff relation", is *not* valid for any arbitrary facet/step orientations 1 and 2. The relationship is *only* valid at the orientations corresponding to maxima or minima in β, i.e. $\dot{R} = 0$, as can be seen from Eqs. (17a) and (17b).

We illustrate the applicability of Eqs. (17a) and (17b) to 2D island shapes that are commonly observed on solid surfaces. Figs. 2a–d are polar plots $R(\theta)$ of square, rectangular, hexagonal, and triangular islands obtained using simple functions of the form $R(\theta) \equiv 15 + \sin(4\theta)$, $R(\theta) \equiv 15 + 3\cos(2\theta)$, $R(\theta) \equiv 30 + \sin(6\theta)$, and $R(\theta) \equiv 10 + \sin(3\theta)$, respectively. From $R(\theta)$, relative values of $\beta(\varphi)$ can be derived using Eqs. (17a) and (17b). The grey curves shown in Fig. 2 are plots of calculated $\beta(\varphi)$ data obtained with $\lambda = 1$.

From Eqs. (17a) and (17b), it can be shown that the step-edge stiffness, $\tilde{\beta}(\varphi) \equiv \beta(\varphi) + \beta''(\varphi)$, where each prime denotes a derivative with respect to φ, is related to the equilibrium island shape $R(\theta)$ through the expression

$$\tilde{\beta}(\varphi) = \frac{\lambda}{\kappa(\theta)} \tag{18a}$$

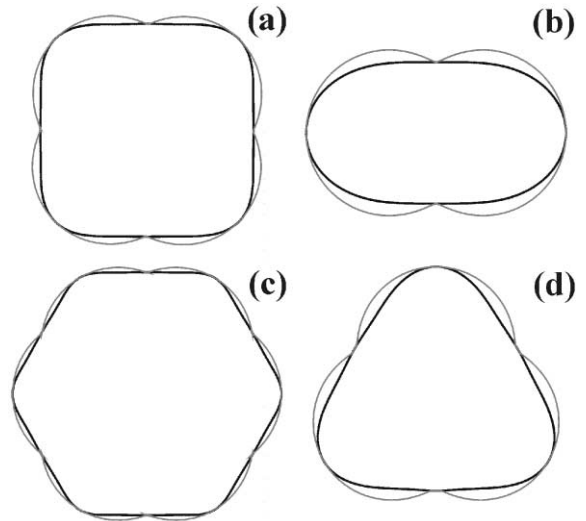for which the curvature $\kappa(\theta)$ of the equilibrium shape is defined as

Fig. 2. Wulff plots, β vs. φ, for commonly observed 2D island shapes $R(\theta)$ on surfaces of cubic materials: (a) fourfold, (b) twofold, (c) sixfold, and (d) threefold symmetric island shapes. The black curves represent the equilibrium island shape functions $R(\theta)$, while the grey curves correspond to $\beta(\varphi)$ obtained analytically using Eqs. (17a) and (17b) with λ set to unity.

$$\kappa(\theta) = \frac{(R^2 + 2\dot{R}^2 - R\ddot{R})}{(R^2 + \dot{R}^2)^{3/2}}. \tag{18b}$$

A microscopic approach such as the Ising model can be used to calculate $\beta(\varphi)$ directly, from which one can predict island equilibrium shapes $R(\theta)$. This is achieved using Eq. (11) to obtain the relation $\beta'(\varphi)/\beta(\varphi) = \dot{R}(\theta)/R(\theta)$ which, together with Eqs. (17a) and (17b), yields the inverse transforms:

$$R(\theta) = \left(\frac{1}{\lambda}\right)\sqrt{\beta^2(\varphi) + (\beta'(\varphi))^2} \tag{19a}$$

and

$$\theta = \varphi + \arctan\left(\frac{\beta'(\varphi)}{\beta(\varphi)}\right). \tag{19b}$$

Thus far, we have shown that relative $\beta(\varphi)$ values can be derived analytically from $R(\theta)$, and conversely, $R(\theta)$ can be obtained from $\beta(\varphi)$. Some of these results have been derived earlier using different approaches [2,3]. The present approach however presents results in generalized coordinates that may be adapted to suit the symmetry of the shapes experimentally encountered, as demonstrated for the cases with Cartesian, spherical, and cylindrical symmetry. However, it is still necessary to determine λ in order to obtain absolute step energies. In the following section, we derive the theory of anisotropic shape fluctuations in order to determine absolute $\beta(\varphi)$ values from measurements of temporal fluctuations about 2D equilibrium shapes of both isotropic and highly anisotropic islands.

4. Anisotropic 2D island shape fluctuation analysis

Time-dependent thermal fluctuations about the equilibrium island shape are due to changes in the total step free energy of the island. Khare and Einstein [16] derived a formalism relating shape fluctuations to the step energy for isotropic (circular) islands. This approach was extended and used to determine average step energies on Cu(1 1 1), Ag(1 1 1), and Cu(0 0 1) [12]. The methodology is restricted however, to the case of isotropic, or near-isotropic, island shapes [12,16].

Many solid surfaces, such as Pb(1 1 1) [4,8], Si(0 0 1) [5], TiN(0 0 1) [13], and TiN(1 1 1) [14], exhibit equilibrium shapes which are highly anisotropic. Here, we proceed by developing a general theory applicable to both anisotropic and isotropic islands. Our approach combines the analytical Wulff construction, described in the previous section, with temporal fluctuations about equilibrium island shapes to determine λ and, hence, absolute orientation-dependent step energies. The symbols R and r in the following discussion refer to the equilibrium island shape $R(\theta)$ and the time-dependent fluctuating shape $r(\theta, t)$. Fig. 3 is a schematic diagram illustrating R and r for an anisotropic hexagonal-shaped island, as observed on TiN(1 1 1) [14].

The total free energy $F(t)$ of an island is related to the island shape r through the relationship

$$F(t) = \int_0^{2\pi} \mathrm{d}\theta\{\beta[\varphi(\theta, t)](r^2 + \dot{r}^2)^{1/2}\}. \tag{20}$$

$\varphi(\theta, t)$ in Eq. (20) is the angle between the local normal to the fluctuating shape at $r(\theta, t)$ and the x-axis as shown in Fig. 3. This is in contrast to Eq. (17a), where $\varphi(\theta)$ corresponds to the local normal to the equilibrium shape at $R(\theta)$. Thus, $\beta(\varphi)$ in Eq. (20) is also a function of r and t. Since the equilibrium shape corresponds to the minimum free energy F_0, temporal deviations $g(\theta, t)$ from the equilibrium shape result in a change in free energy $\Delta F(t) \equiv F(t) - F_0$, where we have defined $g \equiv g(\theta, t)$ (as in Refs. [12,16]) to be the normalized
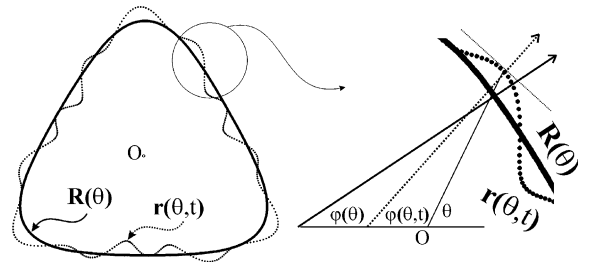

Fig. 3. Schematic diagram of the 2D equilibrium shape $R(\theta)$ of an anisotropic island together with the time-dependent shape $r(\theta, t)$. The center of mass of the island is at O. The inset on the right shows the step orientations $\varphi(\theta)$ and $\varphi(\theta, t)$, as the angles made by the normals to the curves $R(\theta)$ and $r(\theta, t)$ with the horizontal line respectively. $\theta = 0$ is along the horizontal line.

deviation of the temporal shape r from the equilibrium shape R. Thus,

$$g \equiv [r - R]/R. \tag{21}$$

In order to derive an expression for λ in terms of the measurable quantity g, we construct a function $f \equiv f(\theta, r, \dot{r})$ as

$$f(\theta, r, \dot{r}) = \beta[\varphi(\theta, t)](r^2 + \dot{r}^2)^{1/2} - \lambda(r^2/2) \tag{22}$$

such that $F(t) = \int_0^{2\pi} \mathrm{d}\theta[f(\theta, r, \dot{r})]$. The second term in Eq. (22) accounts for the constant area constraint with the Lagrange multiplier λ. Expanding f to second order in r and $\dot{r}$ by Taylor's theorem and neglecting higher order terms, we obtain

$$f(\theta, r, \dot{r}) = f^0(\theta, r, \dot{r}) + f^1(\theta, r, \dot{r}) + f^2(\theta, r, \dot{r}), \tag{23}$$

where the superscripts to the function f denote the order of differentiation. [1] For the equilibrium island shape ($r \equiv R$, and $\dot{r} \equiv \dot{R}$), φ and β are given by Eqs. (17a) and (17b). Thus, from Eq. (22), $f^0(\theta, r, \dot{r}) = (\lambda R^2)/2$. We note that $f^1(\theta, r, \dot{r}) = 0$ is the stability condition for equilibrium. Upon simplification, [2] with β and $\tilde{\beta}$ expressed in terms of

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[1] We define:

$$f^1(\theta, r, \dot{r}) \equiv (r - R)\left[\frac{\partial f}{\partial r}\right] + (\dot{r} - \dot{R})\left[\frac{\partial f}{\partial \dot{r}}\right]$$

and

$$f^2(\theta, r, \dot{r}) \equiv \frac{1}{2}\left\{(r - R)^2\left[\frac{\partial^2 f}{\partial r^2}\right] + (\dot{r} - \dot{R})^2\left[\frac{\partial^2 f}{\partial \dot{r}^2}\right] + 2(r - R)(\dot{r} - \dot{R})\left[\frac{\partial^2 f}{\partial r \partial \dot{r}}\right]\right\},$$

where all the partial derivatives in rectangular brackets are evaluated at $r = R$ and $\dot{r} = \dot{R}$.

[2] We obtain:

$$\frac{\partial f}{\partial r} = \left(-\lambda r + \frac{\beta[\varphi(\theta, t)]r}{(r^2 + \dot{r}^2)^{1/2}} + \frac{\dot{r}}{(r^2 + \dot{r}^2)^{1/2}}\frac{\partial \beta}{\partial \varphi}\right);$$

$$\frac{\partial f}{\partial \dot{r}} = \left\{\beta \dot{r} - \left(\frac{\partial \beta}{\partial \varphi}\right)r\right\}\frac{1}{(r^2 + \dot{r}^2)^{1/2}};$$

$$\frac{\partial^2 f}{\partial r^2} = \left(-\lambda + \frac{\tilde{\beta}(\varphi)\dot{r}^2}{(r^2 + \dot{r}^2)^{3/2}}\right);$$

$$\frac{\partial^2 f}{\partial \dot{r}^2} = \left(\frac{\tilde{\beta}(\varphi)r^2}{(r^2 + \dot{r}^2)^{3/2}}\right); \quad \frac{\partial^2 f}{\partial r \partial \dot{r}} = \frac{-\tilde{\beta}(\varphi)r\dot{r}}{(r^2 + \dot{r}^2)^{3/2}}.$$

R and λ according to Eqs. (17a)–(18b), Eq. (23) reduces to

$$f(\theta, r, \dot{r}) = \frac{\lambda R^2}{2}\left\{1 + \frac{R^2\dot{g}^2}{(R^2 + 2\dot{R}^2 - R\ddot{R})} - g^2\right\}. \tag{24}$$

Thus, the fluctuating component of the free energy functional $\Delta F(t)$ is given by

$$\Delta F(t) = -\lambda \int_0^{2\pi} \mathrm{d}\theta(P(\theta)g^2 - X(\theta)\dot{g}^2) \tag{25a}$$

with functions $P(\theta)$ and $X(\theta)$ defined as

$$P(\theta) \equiv \frac{R^2}{2} \tag{25b}$$

and

$$X(\theta) \equiv \frac{R^4}{2(R^2 + 2\dot{R}^2 - R\ddot{R})}. \tag{25c}$$

Representing the functions $g(\theta)$, $P(\theta)$, and $X(\theta)$, as Fourier series $g(\theta) = \sum_n g_n(t)\mathrm{e}^{\mathrm{i}n\theta}$, $P(\theta) = \sum_n P_n\mathrm{e}^{\mathrm{i}n\theta}$, and $X(\theta) = \sum_n X_n\mathrm{e}^{\mathrm{i}n\theta}$, respectively, Eq. (25a) can be written in terms of the Fourier components $g_n(t)$, X_n, and P_n as

$$\Delta F(t) = -2\pi\lambda \sum_{m,n}[P_{-n-m} + (mn)X_{-n-m}]g_m(t)g_n(t). \tag{26}$$

We note that P_{-n-m} and X_{-n-m} in Eq. (26) are independent of time; temporal changes in the total free energy are only due to $g_n(t)$ and $g_m(t)$. From the definition of g in Eq. (21), $\langle g(\theta, t)\rangle \equiv g_0(t) \equiv 0$. Thus, for fluctuation modes with either $m = 0$ or $n = 0$, the summations in Eq. (26) are equal to zero. Furthermore, under complex conjugation (denoted by superscript *), $g_n^*(t) \equiv g_{-n}(t)$, $P_n^* \equiv P_{-n}$, and $X_n^* \equiv X_{-n}$ guarantee that the functions g, P, and X are all real. Since $\Delta F(t)$ is a homogeneous second-order function in $\{g_n(t)\}$ (i.e., $\Delta F(\{\xi g_n\}) = \xi^2 \times \Delta F(\{g_n\})$, where $\{g_n\}$ denotes $g_n(t)$ at all allowed values of n and ξ is any arbitrary scaling parameter), Euler's theorem [18] requires

$$\sum_n g_n(t)\left[\frac{\partial \Delta F}{\partial g_n}\right] = 2\Delta F(t). \tag{27}$$

According to the generalized equipartition theorem [18], a Hamiltonian $H(\{x_n\})$ which is a homogeneous function of $\{x_n\}$ satisfies the condition

$$\left\langle x_n \frac{\partial H}{\partial x_m} \right\rangle = \delta_{m,n} k_B T, \qquad (28)$$

where x_n represents either canonical momenta p_n or coordinates q_n and $\delta_{m,n}$ is the Kronecker delta function. Ignoring the entropic contribution to the free energy yields $\Delta F \approx \Delta U$, where ΔU is the internal energy of the fluctuating island. Identifying ΔF with H and combining Eqs. (27) and (28), we find that the time-averaged free energy is given by

$$\langle \Delta F \rangle = (N_{\max} k_B T)/2, \qquad (29)$$

where $N_{\max}$ corresponds to the maximum number of allowable fluctuation modes [3] for a finite-sized island. Eliminating $\langle \Delta F \rangle$ from Eqs. (26) and (29), we derive an expression for λ in terms of the experimentally-measurable parameters R and g as

$$\lambda = \frac{-N_{\max} k_B T}{4\pi \langle \sum_{m,n} [P_{-n-m} + (mn)X_{-m-n}] g_m(t) g_n(t) \rangle}. \qquad (30)$$

Eq. (30), together with Eqs. (17a)–(18b), can be used to determine absolute values of $\beta(\varphi)$ and $\tilde{\beta}(\varphi)$. These relations are exact and applicable to both isotropic and anisotropic island shapes. For an isotropic (circular) equilibrium shape, $R(\theta) = R$, a constant. Thus, $P(\theta) = X(\theta) = R^2/2$ and $P_n = X_n = (R^2/4\pi)\delta_{n,0}$. Since the only non-zero terms that contribute to Eq. (30) are those satisfying the condition $m = -n$, we obtain

$$\lambda = \frac{N_{\max} k_B T}{\left(R^2 \sum_n (n^2 - 1) \langle |g_n|^2 \rangle \right)}, \qquad (31)$$

similar to earlier results [4] for isotropic islands [12,16], which were used to relate the fluctuation modes g_n to orientation-averaged step energies.

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[3] If the shortest fluctuation mode corresponds to two surface atoms as in Ref. [12], $N_{\max}$ is defined as one half of the total number of atoms along the island periphery.

[4] The term $(n^2 - 1)$ in Eq. (31) appears as (n^2) in Ref. [16] since they ignored the term arising from the constant area constraint in their analysis.

5. Conclusions

We have derived general expressions in orthogonal curvilinear (with specific solutions in Cartesian, spherical polar, and circular cylindrical) coordinates for surface and step energies from the equilibrium 3D crystal and 2D island shapes, respectively. For 2D islands, explicit relations for the relative orientation-dependent step energies in terms of the equilibrium shape are presented. In order to determine the absolute step energies and step stiffnesses, we have developed a general formalism, exact to second order, for the analysis of shape fluctuations applicable to both isotropic and highly anisotropic islands. Our analysis for 2D islands has been used to extract the absolute orientation-dependent step energies for highly anisotropic islands on TiN(1 1 1) [14].

Acknowledgements

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