Universal Jump of Gaussian Curvature at the Facet Edge of a Crystal

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Novel universal behavior of the equilibrium crystal shape is reported: The Gaussian curvature, a product of two principal curvatures, assumes a universal jump across the facet contour at any temperature below the roughening temperature. This behavior is shown to be a consequence of a universal relation between the coefficients γ_s and B in the small-**p** expansion (**p** is the surface gradient) of the interface free energy, $f(\mathbf{p})=f(0)+\gamma_s|\mathbf{p}|+B|\mathbf{p}|^3+O(|\mathbf{p}|^4)$. Both exact results on a solvable model and Monte Carlo calculations support this behavior—*universal Gaussian-curvature jump* at the facet edge.

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Two universal features are known for the "shape transitions"[1-6] of the equilibrium crystal shape (ECS). One is associated with the faceting transition[1-4] at the roughening temperature T_R. Across T_R the curvature κ of the ECS assumes a *finite jump* whose amount is *universally* given[3] by $\Delta\kappa=(2/\pi)\lambda/k_\mathrm{B}T_R$ (the parameter λ, which will be used throughout this Letter, corresponds to the Lagrange multiplier appearing in the Wulff construction[7-9] and is related[10] to the pressure difference ΔP across the interface or to the chemical potential difference $\Delta\mu$). The other is associated with behavior of the ECS near its facet edge below T_R. Let us take a Cartesian coordinate system such that the x-y plane is parallel to the facet with the origin at the center of the facet. The ECS is described by an equation $z=z(x,y)$. The profile of the curved region along the x axis, then, behaves[3] as $z\sim(x-x_c)^{3/2}$ $(x>x_c)$ near the facet edge $x=x_c$. This implies the square-root divergence of the longitudinal curvature $\kappa_x\sim d^2z/dx^2\sim(x-x_c)^{-1/2}$, with the exponents $\frac{3}{2}$ and $-\frac{1}{2}$ being the universal values for Gruber-Mullins-Polrovsky-Talapov[11,12] type transitions. These two universal features of the ESC, one at T_R and the other at the facet edge below T_R, are now at the stage of experimental confirmation.[13-20]

In this Letter, we report another novel universal behavior of the ECS, which is to be seen below T_R: At the facet edge, the *Gaussian curvature K*, which is a product of two principal curvatures $[\sim(d^2z/dx^2)d^2z/dy^2$, if the x or y axis is parallel to the crystal axis], jumps from 0 (on the facet side) to a finite value[21] ΔK (on the side of the curved region) with *universal amplitude* given by

$$(k_\mathrm{B}T/\lambda)(\Delta K)^{1/2}=\pi^{-1}. \tag{1}$$

Interestingly, as compared with the known universal jump $k_\mathrm{B}T_R\Delta\kappa/\lambda=2/\pi$ at T_R, we see a factor of 2 difference between $\Delta\kappa$ and $(\Delta K)^{1/2}$. This newly found feature of the ECS is universal in the sense that it is to be observed for *any systems* with short-range interactions, at *any position* on the facet contour, and at *any temperature* below T_R.

By $\gamma(\mathbf{p})$ we denote the orientation-dependent interface tension, where $\mathbf{p}=(p_1,p_2)=(\partial z/\partial x,\partial z/\partial y)$ is the interface gradient vector. The interface free energy per projected area is given by $f(\mathbf{p})=\gamma(\mathbf{p})(1+|\mathbf{p}|^2)^{1/2}$. To discuss the ECS near the facet edge which is governed by small-p behavior of $f(\mathbf{p})$, we consider a vicinal surface with step density $|\mathbf{p}|$ (we take the unit step height to be unity) below T_R. In systems with short-range interactions, we have the following expansion[3,5,11,12,22-27]:

$$f(p)=f(0)+\gamma_s(\theta)|\mathbf{p}|+B(\theta)|\mathbf{p}|^3+O(|\mathbf{p}|^4), \tag{2}$$

where θ is defined by $p_1=-|\mathbf{p}|\cos\theta$, $p_2=-|\mathbf{p}|\sin\theta$. Physically, θ is the angle between the y axis and the direction along which, on average, step lines are running. In the limit $|\mathbf{p}|\to 0$, θ becomes the direction angle of the tangential line of the facet contour (Fig. 1). The coefficient $\gamma_s(\theta)$ in (2) is the per-length step free energy, and the cubic term represents the effect of step-step interactions. The essential point of our argument for (1) is that there exists a *universal relation* between $B(\theta)$ and the "step stiffness" $\gamma_s(\theta)+\gamma_s''(\theta)$,

$$B(\theta)=\pi^2(k_\mathrm{B}T)^2/\{6[\gamma_s(\theta)+\partial^2\gamma_s(\theta)/\partial\theta^2]\}. \tag{3}$$

In fact, assuming relation (3), we obtain (1) as follows. Working with the Legendre-transformed free energy

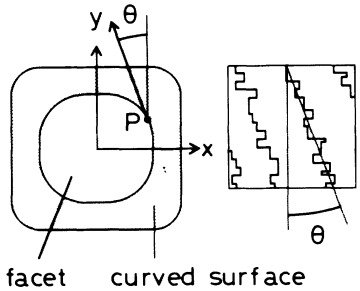

FIG. 1. Left: Top view of a facet, where θ is the direction angle of the tangential line of the facet contour at a point P. Right: Magnified view of the curved surface near the point P. The angle θ corresponds to the mean running direction of the steps on the surface.

$\tilde{f}(\eta)=\min_{\mathbf{p}}[f(\mathbf{p})-\eta\cdot\mathbf{p}]$ which gives[1] the ECS as $\lambda z=\tilde{f}(-\lambda\mathbf{x})$ $[\mathbf{x}=(x,y)]$, we calculate the Gaussian curvature K to be[28]

$$K=\lambda^2(1+|\mathbf{p}|^2)^{-2} \times\{\det[\partial^2 f(\mathbf{p})/\partial p_i\,\partial p_j]\}^{-1}|_{\mathbf{p}=\mathbf{p}(\eta)=\mathbf{p}(-\lambda\mathbf{x})}. \quad (4)$$

Substituting (2) into (4) and taking $|p|\to 0$, we have a limiting value of K approached from the curved region,

$$K=\lambda^2/\{6B(\theta)[\gamma_s(\theta)+\partial^2\gamma_s(\theta)/\partial\theta^2]\}\quad (|\mathbf{p}|\to 0). \quad (5)$$

Inserting (3) into (5), we obtain (1).

We prove relation (3) by taking account of the non-crossing nature of the steps and by careful treatment of the coarse-grained step wanderings. Let us consider a coarse-grained system of size L (x direction or space direction)$\times M$ (t direction or time direction). The time direction is chosen to be the mean running direction of steps. Note that crossings of steps are virtually forbidden since they inevitably produce significant areas of "overhangs" which are energetically unfavorable. Therefore, we can regard the steps as continuous lines describing space-time trajectories of Browian particles with *hard-core repulsion.* In terms of the transfer-matrix method, the system is equivalent to the impenetrable Bose gas, which allows us to take the free fermion approach.[5,22–27,29] Writing the transfer matrix for the continuous system as $\exp(-\beta H)$ $(\beta=1/k_\mathrm{B}T)$, we have the following expression for the Hamiltonian H:

$$H=Lf(0)+\int_0^L dx\left[\mu a^\dagger(x)a(x)+\frac{\alpha}{2}\frac{\partial a^\dagger(x)}{\partial x}\frac{\partial a(x)}{\partial x}\right], \quad (6a)$$

$$\equiv Lf(0)+\mu N+H_K, \quad (6b)$$

where $a^\dagger(x)$ and $a(x)$ are spinless fermion operators, N the particle number operator, and H_K the kinetic-energy operator. The partition function Z_n for the n-step sector is expressed as

$$Z_n=\sum\langle \text{final};n\,|\,[\exp(-\beta H)]^M\,|\,\text{initial};n\rangle,$$

where the sum is over all possible initial and final states of n particles. The free energy

$$f(\mathbf{p})=-\lim_{L,M\to\infty}(k_\mathrm{B}T/LM)\ln Z_n,$$

with fixed particle number density $|\mathbf{p}|=n/L$, is given by the energy density of the ground state (Fermi vacuum):

$$f(p)=f(0)+\mu|\mathbf{p}|+\alpha(\pi^2/6)|\mathbf{p}|^3. \quad (7)$$

Comparing (7) with (2), we have the identification[30]

$$\mu=\gamma_s(\theta),\quad \alpha\pi^2/6=B(\theta), \quad (8)$$

which means that μ and α are not microscopic parameters but are macroscopic quantities due to the coarse graining. Further, inspection on the "one-body" problem leads to a relation between μ and α. Suppose that there is only one step on the x-t plane. We specify the space-time position of the step by the coordinates (x,t) $(0\le x\le L,\ 0\le t\le M)$ and assume that the step "starts" at $(x_0,0)$ $(x_0\sim L/2)$. The probability distribution function $P(\Delta x)$ for finding the end point of the step at $(x_0+\Delta x,M)$ is known to be Gaussian, $P(\Delta x)\sim\exp[-(\Delta x)^2/2M\sigma^2(\theta)]$, where $\sigma(\theta)$ is calculated from (6) as

$$\sigma^2(\theta)=\beta\alpha. \quad (9)$$

We should then recall a relation[31–34]

$$\sigma(\theta)^{-2}=\beta[\gamma_s(\theta)+\gamma_s''(\theta)], \quad (10)$$

where we have regarded $\sigma(\theta)$ as the *scaled fluctuation width* of a one-dimensional interface. Combining (8), (9), and (10), we obtain the desired relation (3).

Let us see that, for a given value of θ, the relation (3) actually holds for an exactly solvable model, Beijeren's body-centered-cubic solid-on-solid (BCSOS) model[35] which is a special case of the six-vertex model[36] (Rys's F model). We denote the excitation energy of the F model by J and introduce a parameter ω (≥ 0) by $2\cosh\omega=\exp(2J/k_\mathrm{B}T)-2$. For $\theta=0$, i.e., along the crystal axis of the BCSOS model, we have[36]

$$B(0)=k_\mathrm{B}T\frac{\pi^2}{6}\frac{Z''(\omega)}{Z'(0)^2}, \quad (11)$$

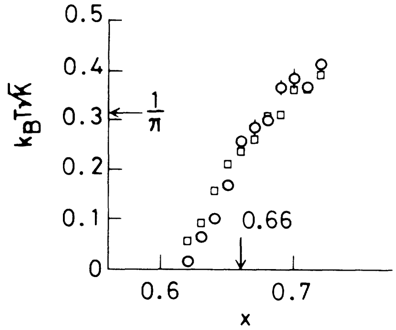

FIG. 2. Monte Carlo results on the absolute SOS model in a field with system sizes 54×54 (squares) and 80×80 (circles) for $k_BT/J=0.7$. Gaussian curvature K of the normalized ECS ($\lambda=1$) along the x direction is calculated as a function of the x coordinate [=(field strength)/J]. Each point represents an average over 1.8×10^6 Monte Carlo steps per site. From the interface tension of the two-dimensional Ising model, the facet-edge position is approximately estimated to be $x_c=0.66$. Because of the finite-size rounding, the expected discontinuous change of K is somewhat smeared out. The calculated value of $k_BT\sqrt{K}$ at x_c is slightly smaller than, but consistent with, the universal value $1/\pi$ ($=0.32$). A clear tendency is seen for increasing system size to lead to better agreement with the predicted behavior.

where the function $Z(\phi)$ ($|\phi|\le 2\omega$) is defined as

$$Z(\phi)=\ln\frac{\cosh\frac{1}{2}(\omega+\phi)}{\cosh\frac{1}{2}(\omega-\phi)}-\tfrac{1}{2}\phi-\sum_{n=1}^{\infty}\frac{(-1)^n e^{-2n\omega}\sinh n\phi}{n\cosh\omega}. \quad (12)$$

We should remark here that the shape of the facet contour is a two-dimensional ECS[37] which is determined from $\gamma_s(\theta)$ regarded as a one-dimensional anisotropic interface tension. Then we can calculate the step stiffness $\gamma_s(\theta)+\gamma_s''(\theta)$ from the curvature of the facet contour.[28,32] From the equation for the facet contour[3,38]

$$\lambda x=-k_BTZ(\omega+\phi),\quad \lambda y=-k_BTZ(\phi), \quad (13)$$

we obtain step stiffness for $\theta=0$ (i.e., $y=0$, $\phi=0$) as

$$\gamma_s(0)+\gamma_s''(0)=\left[\frac{d^2(\lambda x)}{d(\lambda y)^2}\right]^{-1}\Bigg|_{\phi=0}=k_BT\frac{Z'(0)^2}{Z''(\omega)}. \quad (14)$$

Combining (11) and (14), we confirm the relation (3) and the universal Gaussian-curvature jump (1) for $\theta=0$.

As a test for (1), we performed Monte Carlo calculations on the absolute SOS model with coupling constant[39] J ($k_BT_R/J=1.24$) under the free boundary condition, where an external field is applied to maintain the average tilt.[40] The "fluctuation-geometry" relation[28] allow us to evaluate the curvature tensor of the ECS from the correlations among the gradient fluctuations $\{\Delta p_i\}$ ($i=1,2$). We calculated the Gaussian curvature for the "normalized" ECS with $\lambda=1$, along the x direction. In Fig. 2, we have plotted $k_BT\sqrt{K}$ vs x [in Fig. 2 x is (field strength)/J] for $k_BT/J=0.7$. The facet-edge position is estimated from the interface tension of the two-dimensional Ising model,[41] regarded as the approximate step free energy. The results are consistent with (1).

To summarize, we have shown that there occurs a universal jump of the Gaussian curvature at the facet edge of a crystal at all temperatures below T_R. We have presented an argument based on the terrace-step-kink picture of the vicinal surface, taking account of the short-range repulsive (impenetrable) nature of the step-step interactions and the correct coarse-grained fluctuation property of a single step. The novel universal behavior is confirmed both by exact results on the BCSOS model and by Monte Carlo calculations on the absolute SOS model.

As further confirmation, both experimental observations and theoretical calculations on other models are welcome.

A full account of this Letter, including detailed calculations on the solvable models (generalized terrace-step-kink model[42] and the BCSOS model) and further Monte Carlo results on the absolute SOS model will be published elsewhere.[43]

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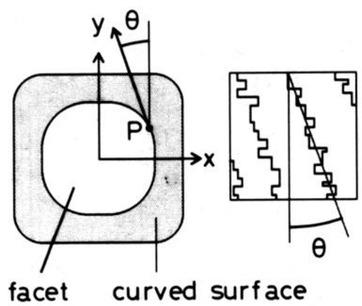

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