Fluctuations of an Atomic Ledge Bordering a Crystalline Facet

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When a high symmetry facet joins the rounded part of a crystal, the step line density vanishes as $\sqrt{r}$ with r denoting the distance from the facet edge. This means that the ledge bordering the facet has a lot of space to meander as caused by thermal activation. We investigate the statistical properties of the border ledge fluctuations. In the scaling regime they turn out to be non-Gaussian and related to the edge statistics of GUE random matrices.

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Equilibrium crystal shapes typically consist of various flat facets connected by rounded surfaces. For a microscopically flat facet there must be an atomic ledge bordering the facet. This border step could be blurred because of thermal excitations, but is clearly visible at sufficiently low temperatures [1–3]. While in the interior of the rounded piece of the crystal the step line density is of order one on the scale of the lattice constant, it decays to zero as the edge of a high symmetry facet is approached. If r denotes the distance from the facet edge, according to Pokrovsky-Talapov [4] the step line density vanishes as $\sqrt{r}$. Thus there is a lot of space for the border ledge to meander, in sharp contrast to steps in the rounded part which are so confined by their neighbors that they fluctuate only logarithmically [5]. The goal of our letter is to explore quantitatively the statistics of border ledge fluctuations. To illustrate our set-up we display in Figure 1 a typical configuration from a statistical mechanics model which will be discussed towards the end of the letter. One clearly recognizes the three facets as joined through a single rounded piece. Our interest is the statistics of the uppermost ledge.

Experimentally ledge fluctuations are an elegant tool to determine step energies [3, 6]: One carefully prepares an island, linear size L, of single atom height on a high symmetry facet. Alternatively, one sputters an undercut island. The ledge bordering the island fluctuates like a closed random walk along the perimeter of the island, which implies fluctuations of size $\sqrt{L}$ [7]. In contrast, for the edge step of a facet there is a delicate balance between its own line tension and the entropic repulsion due to the neighboring ledges in the rounded part, which results in non-Gaussian fluctuations of size $L^{1/3}$. As an important consequence, the border ledge meanders unconstrained over many lattice units and one expects, as well established for random walks, that its large scale statistics is universal with a scale set by material parameters like the local mean square displacement. In fact, we will develop such a scaling theory where the material specific properties enter only through two independent coefficients.

Before considering a facet edge we remind the reader of the terrace-ledge-kink (TLK) model, which serves as a rather accurate description of a vicinal surface, i.e. a crystal cut at a small angle relative to a high symmetry crystal plane. The surface is made up of an array of ledges which on the average run in parallel and are separated by terraces. The ledges are not perfectly straight and meander through kink excitations, only constrained not to touch a neighboring ledge. One can think of these ledges also as discrete random walks constrained not to cross, i.e. with a purely entropic repulsion. Such a line ensemble is very close to Dyson's Brownian motion, in which the random walks are replaced by continuum Brownian motions. As discussed already in [8, 9], the location of the steps at fixed random walk time t have the same distribution as the eigenvalues of a GUE ($\beta = 2$) random matrix. On this basis it is expected that the ledge-ledge distance is governed by the GUE level spacing [10]. This prediction is verified experimentally [11], however with deviations from $\beta = 2$ which are attributed to long range elastic forces mediated through the bulk of the crystal and not included in the TLK model.

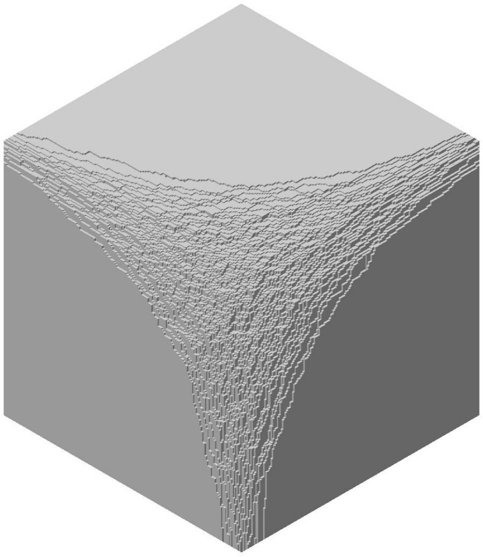

FIG. 1: *Crystal corner viewed from the* [111]*-direction.*

If in the TLK model one retains the lattice structure

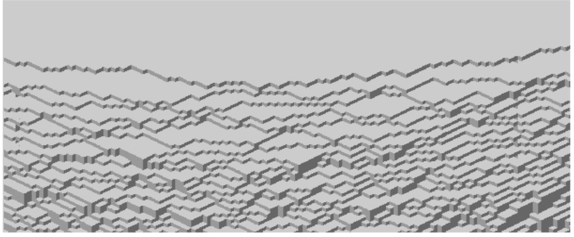

FIG. 2: *Zoom to the facet edge in Figure 1.*

in the transverse direction and makes the continuum approximation in the direction along the ledges, then the ledges can be regarded as the world lines of free fermions in space-time $\mathbb{Z} \times \mathbb{R}$ [12]. The world lines are piecewise constant and have jumps of one lattice unit at most. Consequently the transfer matrix has a nearest neighbor hopping term and the Pauli exclusion principle guarantees that the ledges never cross. In this standard version, the TLK model is translation invariant with constant step density.

In Figure 2 we show an enlargement of the steps near the upper facet edge. Locally an isolated ledge looks like a random walk, and if on disregards the systematic curvature, the ledges are only constraint by entropic repulsion. These two features are shared by the TLK model, whose step stiffness can be adjusted simply by rescaling the continuous axis. Thus the ‘world lines’ in the lower part of the figure are in essence described by the TLK model. The transfer matrix operates from left to right, i.e. fermionic time corresponds to the continuous axis of the TLK model. However at the facet edge the step density is not uniform and, clearly, there is a last ledge. To account for such properties, the natural guess is that on top of the entropic repulsion the steps are subject to an additional external potential, which close to the edge is approximately linear. We will first explore this simple ansatz and explain later on how it is the result of a more involved analysis of statistical mechanics models. The transfer matrix is written in exponential form as $e^{-tH_{\mathrm{F}}}$ with generator H_{F} given by the fermionic Hamiltonian

$$H_{\mathrm{F}} = \sum_j \big(- a_j^\dagger a_{j+1} - a_{j+1}^\dagger a_j + 2 a_j^\dagger a_j + \frac{j}{\lambda} a_j^\dagger a_j \big) . \quad (1)$$

The creation/annihilation operators $a_j^\dagger, a_j$ satisfy the anticommutation relations $\{a_i, a_j^\dagger\} = \delta_{ij}$, $\{a_i, a_j\} = 0 = \{a_i^\dagger, a_j^\dagger\}$. The first two terms of (1) are the nearest neighbor hopping, while the last two terms fix a chemical potential which depends linearly on the position of the fermions and has slope $\lambda^{-1} > 0$. λ controls how rapidly the facet crosses over into the rounded part. Since this variation is on a scale much larger than the lattice spacing, λ is very large and we will study the idealized limit $\lambda \to \infty$. In our simplified model ledges extend to $\pm\infty$ without any curvature, which requires to consider the ground state for (1).

Each ledge is associated with a fermion. Then the average step line density equals the average fermion density in the ground state. Using the eigenfunction expansion for the one-particle Hamiltonian of (1) this density has been computed in [13] with the result

$$\begin{aligned} \rho_\lambda(j) = \langle a_j^\dagger a_j \rangle_\lambda \;&=\; \lambda\big(L_{j-1+2[\lambda]}(2\lambda) J_{j+2[\lambda]}(2\lambda) \\ &\quad - L_{j+2[\lambda]}(2\lambda) J_{j-1+2[\lambda]}(2\lambda)\big) \end{aligned} \quad (2)$$

where $[\lambda]$ denotes the integer part of λ, $J_j(z)$ the Bessel function of integer order j, and $L_j(z) = (d/dj) J_j(z)$. For large λ, on a rescaled lattice with lattice constant λ^{-1}, $\rho_\lambda(\lambda r)$ tends to a limit, which yields the macroscopic crystal shape

$$h_{\mathrm{ma}}(t,r) = \begin{cases} (r+2) \quad \text{for } r \le -4\,, \\ \frac{1}{\pi}\Big((r+2) \arccos(\frac{r+2}{2}) \\ \quad - \sqrt{4-(r+2)^2} \Big) \quad \text{for } -4 \le r \le 0\,, \\ 0 \quad \text{for } r \ge 0\,. \end{cases} \quad (3)$$

h_{ma} is independent of t, which reflects that curvature effects have been ignored, so far, and results from a transfer matrix homogeneous in t. The lower facet edge is located at $r = 0$, which a posteriori is the reason for adding in (1) a constant chemical potential. By construction our model can be trusted only near the facet edge. To check, one expands in (3) near $r = 0$ with the result $h_{\mathrm{ma}}(r,t) \cong -\frac{2}{3\pi}(-r)^{3/2}$. Pokrovsky-Talapov is satisfied, as it should be.

The reader will have noticed that in (1) we left out kink energies and other dimensional constants. This is only to make our argument more transparent. In the final result below material properties of the crystal will appear.

We now refine the resolution and first consider the step density close to $r = 0$. The correct scale is $\lambda^{1/3}$ lattice constants. As explained in [13], one finds

$$\lim_{\lambda\to\infty} \lambda^{1/3} \rho_\lambda(\lambda^{1/3} x) = -x \mathrm{Ai}(x)^2 + \mathrm{Ai}'(x)^2 \,, \quad (4)$$

Ai the Airy function. (4) has the asymptotics

$$\begin{aligned} &\frac{1}{\pi}\sqrt{|x|} \quad \text{for} \quad x \to -\infty\,, \\ &\frac{1}{8\pi x} \exp(-4x^{3/2}/3) \quad \text{for} \quad x \to \infty\,. \end{aligned} \quad (5)$$

Thus the $\sqrt{r}$ law is interpolated by an Airy like function. It could be of advantage to use (4) as a fit to STM data from small crystallites.

$\rho_\lambda(\lambda^{1/3} x)$ has plateaus at the zeros of the Airy function, which allows to roughly identify the average position of individual ledges. In particular, the last ledge meanders close to the origin with lateral excursions of order $\lambda^{1/3}$. Let $b_\lambda(t)$ be the location of the border ledge, where as before t refers to the longitudinal direction (=

fermionic time). $b_\lambda(t)$ takes integer values and is piecewise constant with unit kinks. The index λ should remind us that the statistics of the border ledge depends on λ. From the fermion representation one infers that the single time distribution, i.e. the distribution of the transverse location of the edge step in Figure 2, can be computed as

$$\mathrm{Prob}(\{b_\lambda(0) \le a\}) = \det(1 - P_a B^\lambda) \tag{6}$$

with P_a the projection operator on the interval $[a, \infty)$ and B^λ the discrete Bessel kernel, $B^\lambda_{ij} = \sum_{l \le [2\lambda]} J_{i-l}(2\lambda) J_{j-l}(2\lambda)$. Under rescaling with $\lambda^{1/3}$, (6) goes over to

$$\lim_{\lambda \to \infty} \mathrm{Prob}(\{b_\lambda(0) \le \lambda^{1/3} a\}) = \det(1 - P_a K)\,. \tag{7}$$

The one-particle operator K can be guessed from the continuum approximation to (1), which yields as one-particle Hamiltonian the Airy operator

$$H = -\frac{d^2}{dx^2} + x\,. \tag{8}$$

K is then the projection operator onto all states with $H \le 0$, explicitly as kernel in position space

$$K(x,y) = (x-y)^{-1}\big(\mathrm{Ai}(x)\mathrm{Ai}'(y) - \mathrm{Ai}'(x)\mathrm{Ai}(y)\big)\,, \tag{9}$$

which is the Airy kernel. (7) is the well known Tracy-Widom distribution for the largest eigenvalue of a GUE random matrix in the limit $N \to \infty$ [14]. In view of the connection between ledge spacings and energy level spacings inside the rounded piece such a result is not so surprising.

(7) provides very precise information on the transverse statistics. An even more obvious quantity of interest is the two-point ledge variance $\langle [b_\lambda(t) - b_\lambda(0)]^2 \rangle$, for which one needs the two-point function of the border ledge. From (7) the one-point fluctuations are of order $\lambda^{1/3}$. According to the random walk picture one expects $(\mathit{space})^2 \sim \mathit{time}$ and hence the longitudinal scale to be of order $\lambda^{2/3}$. Through fermionic techniques one obtains, for $\tau > 0$,

$$\begin{aligned} &\lim_{\lambda \to \infty} \mathrm{Prob}(\{b_\lambda(0) \le \lambda^{1/3} a\,, b_\lambda(\lambda^{2/3}\tau) \le \lambda^{1/3} b\}) \qquad (10)\\ &= \det(1 - P_a K - e^{-\tau H} P_b e^{\tau H} K + P_a e^{-\tau H} P_b e^{\tau H} K) \end{aligned}$$

with H of (8) and K the Airy kernel. The average of $(a-b)^2$ with respect to the distribution function (10) defines the scaling function $g(\tau)$ and the limit in (10) implies

$$\mathrm{Var}\big(b_\lambda(t) - b_\lambda(0)\big) \cong \lambda^{2/3} g(\lambda^{-2/3} t), \tag{11}$$

for large λ, with $\mathrm{Var}(b) = \langle (b - \langle b \rangle)^2 \rangle$. The scaling function $g(\tau)$ behaves as

$$g(\tau) \simeq \begin{cases} 2|\tau| & \text{for } \tau \ll 1. \\ g(\infty) - c\,\tau^{-2} & \text{for } \tau \gg 1. \end{cases} \tag{12}$$

(11) together with (12) is our central novel result. $g(\infty) = 1.6264$ is two times the variance of the GUE Tracy-Widom distribution and is known numerically with very high precision, c is estimated from Monte-Carlo data roughly as 1.5 ± 0.3.

At this stage the linear chemical potential in (1) is merely an educated guess. We still have to confirm it through the analysis of microscopic models. In [13] we studied the case where the ledges are pinned at $t = \pm T$ to occupy all sites from 0 down to $-\infty$ and otherwise they have purely entropic repulsion. This produces a as seen from the facet negatively curved edge. Subtracting the mean curvature and considering only the ledges close to the facet edge yields in the limit $T \to \infty$ the statistics from (7), (10) for the border ledge. When viewed as a model for a real crystal facet the pinning at $\pm T$ is somewhat artificial. As a more convincing choice we thus consider the Ising corner, a simple cubic crystal which occupies the positive octant of $\mathbb{Z}^3$, see Figure 1. Allowed crystal configurations are obtained by removing atoms successively such that each time exactly three bonds are broken. Thus our model is the lattice gas version of the 3-dimensional Ising model at zero temperature respecting specific boundary conditions. Under volume constraint the number, N, of removed cubes, is fixed and every crystal configuration is equally likely. Figure 1 is a single sample with $N \simeq 300\,000$. As noted in [15], this model can still be analyzed through fermionic techniques. For $N \to \infty$ there is a definite macroscopic shape, which has (100), (010), and (001) as three high symmetry facets. They are joined by a rounded surface satisfying Pokrovsky-Talapov. Analytic formulae for the macroscopic shape are available [16]. We record here only the macroscopic position of the (001) facet edge, $b_\infty(\tau) = -\ln(1 - e^{-\tau})$, $\tau > 0$, with coordinates along the [100] and [010] directions.

We introduce the scaling parameter ℓ by $N = \frac{1}{4}\zeta(3)\ell^3$, $\zeta(3) = 1.202\ldots$ being Apery's constant. The atomic border ledge position in the (001) plane is given by $b_\ell(x)$, $x = 0, 1, 2, \ldots$. $b_\ell(x)$ takes positive integer values and is decreasing as $b_\ell(x+1) \le b_\ell(x)$. The ledge has only South and East turns and meanders close to its asymptotic mean $\ell b_\infty(x/\ell)$. We zoom at the fixed macroscopic edge point $(\ell\tau, \ell b_\infty(\tau))$, $\tau > 0$. Upon proper rescaling [17], one recovers exactly the same statistics as in (10). More precisely, for large ℓ,

$$\mathrm{Var}\big(b_\ell(\ell\tau + x) - b_\ell(\ell\tau)\big) \cong (A\ell)^{2/3} g\Big(\frac{A^{1/3} x}{2\,\ell^{2/3}}\Big), \tag{13}$$

with $A = b''_\infty(\tau)$. (13) differs from (11) in two respects. Firstly, to obtain the border ledge fluctuations one has to subtract the systematic mean. Since for our particular model the macroscopic facet edge is explicit, the subtraction is $\langle b_\ell(\ell\tau + x)\rangle - \langle b_\ell(\ell\tau)\rangle \cong b'_\infty(\tau)x + \frac{1}{2}b''_\infty(\tau)\ell^{-1}x^2$ with negligible higher order corrections. Secondly, material properties enter indirectly through A. Since by (12), for small $|x|$, $\mathrm{Var}\big(b_\ell(\ell\tau + x) - b_\ell(\ell\tau)\big) = A|x|$, A is the local wandering, resp. diffusion, coefficient.

We claim that the scaling form (13) holds for any surface model with short range step-step interaction. To properly formulate such universal scaling, we start with a purely thermodynamic argument. Let $h(x,y)$ be the height of a vicinal surface measuring the number of layers relative to a high symmetry reference plane and $k_B T f(\mathbf{u})$ be the surface free energy per unit projected area depending on the local slope $\mathbf{u} = \nabla h$. Below the roughening transition f has a cone at $\mathbf{u} = 0$ and for small $\mathbf{u}$ behaves as

$$f(\mathbf{u}) \cong \gamma(\theta)|\mathbf{u}| + B(\theta)|\mathbf{u}|^3 \tag{14}$$

with θ the polar angle of $\mathbf{u}$ [18]. The line stiffness $\widetilde{\gamma}$ is defined through $\widetilde{\gamma}(\theta) = \gamma(\theta) + \gamma''(\theta)$. As argued in [19] for short range surface models the Gaussian curvature $\det f''$ of the surface free energy has the universal limit π^2 for $\mathbf{u} \to 0$, which implies the relation $\widetilde{\gamma}(\theta)B(\theta) = \pi^2/6$. Let us denote by $\widehat{f}$ the Legendre transform of f. If $\int dxdy f(\nabla h(x,y))$ is minimized under the constraint of fixed volume, then the resulting equilibrium surface is given by $h(x,y) = \ell \widehat{f}(\ell^{-1}x, \ell^{-1}y)$, where ℓ is the Lagrange multiplier adjusted so to give the correct volume. h is convex downwards and has a convex facet lying in the x-y plane. The facet boundary is determined by $\gamma(\theta)$ alone. Close to the facet edge, $h \cong -\frac{2}{3}\gamma_{PT} d^{3/2}$ with d the normal distance to the facet edge, which defines the Pokrovsky-Talapov coefficient γ_{PT}. Under Legendre transformation the angle θ becomes the angle between the x-axis and the outer normal to the facet and, correspondingly, γ_{PT}, the local curvature κ, and the distance r of a point on the edge to the origin are parametrized through this angle θ. The relationship between $\widetilde{\gamma}$ and B implies

$$\gamma_{PT}^2 \kappa = 2\ell^{-2}\pi^{-2}. \tag{15}$$

We return to the border ledge fluctuations close to a given angle θ_0. For this purpose it is convenient to center the x-y axis coordinate system at $r(\theta_0)$ with the x-axis tangential and the y-axis along the inner normal to the facet. In this frame, we denote by $y = b(x)$ the fluctuating border step. Then $\langle b(x)\rangle = \frac{1}{2}\kappa(\theta_0)x^2$, in approximation. For sufficiently small $|x|$, still large on the scale of the lattice, $b(x)$ is like a random walk and $\mathrm{Var}\big(b(x) - b(0)\big) \cong \sigma^2|x|$, which defines the local wandering coefficient σ^2. Following [20] it is natural to equate $\sigma(\theta)^2$ with the inverse stiffness $\widetilde{\gamma}(\theta)^{-1}$.

This implies

$$\sigma^2 = \kappa\ell, \qquad \kappa = \pi^2\gamma_{PT}^2\sigma^4/2 \tag{16}$$

valid for any point on the facet edge. In particular the shape of the facet edge can also be infered from $\sigma(\theta)$. For the Ising corner in the [100]-[010] frame one obtains $A = \sigma^2(1 + \tan^2\theta)^{3/2}$. Thus in the tangential frame the scaling form (13) generalizes to

$$\mathrm{Var}\big(b(x) - b(0)\big) \cong \sigma^{4/3}\ell^{2/3} g\big(\tfrac{1}{2}\sigma^{2/3}\ell^{-2/3}x\big). \tag{17}$$

We emphasize that there are only two independent material parameters, which through (15) and (16) can be reexpressed in terms of κ and γ_{PT}.

As our main novel finding, for surface models with short range interactions, the border ledge of a facet has fluctuations of size $\ell^{1/3}$. Thus they are much reduced in comparison with a simple random walk model. The scaling function g for the variance of the fluctuations is known from our theory. There are two material related constants. Experimentally, we expect that at least the reduction of the fluctuations could be observed. We tested this prediction on the single sample of Figure 1 with encouraging results, of course having the valuable advantage that the surface free energy in known anaytically.

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