Three Tales of Three Scales in Epitaxial Growth:
Lecture I:
On Fundamentals of Crystal Surface Morphological Evolution

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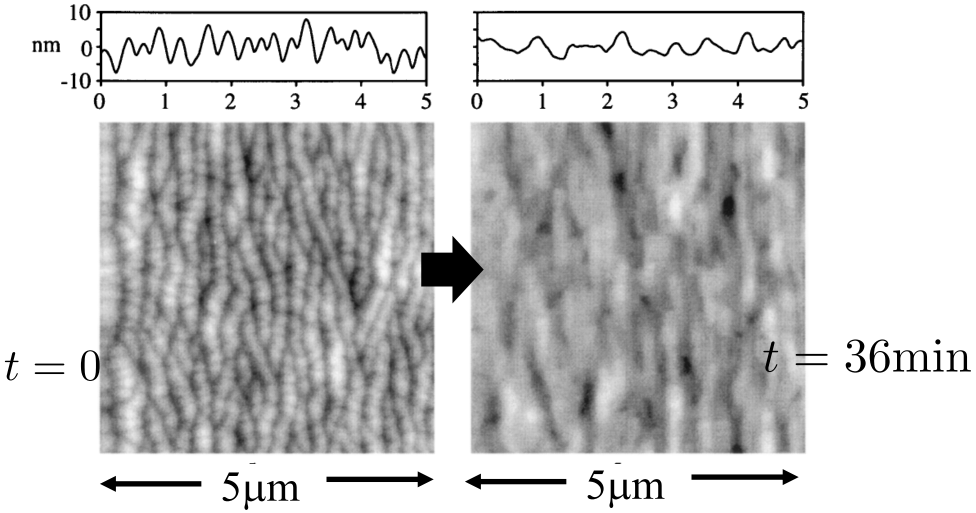
*Research supported by NSF DMS-1412769

Symposium on: Mathematical Aspects of Surface and Interface Dynamics
University of Tokyo, Japan
Wednesday, 17 October 2018

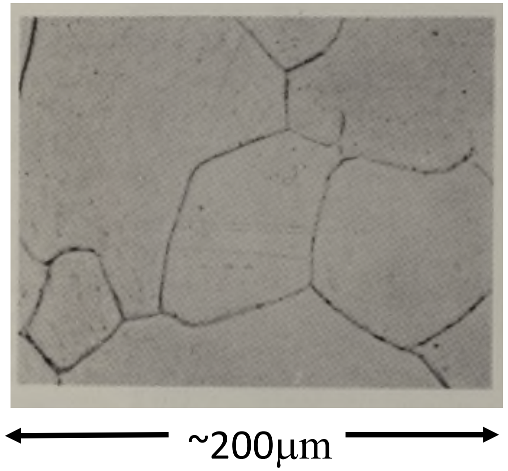
Crystal surfaces out of equilibrium: A sample

"Non-classical" smoothening of
Si surface corrugations (T=667° C)



[Erlebacher, Aziz, Chason, Sinclair, Floro, 2000]

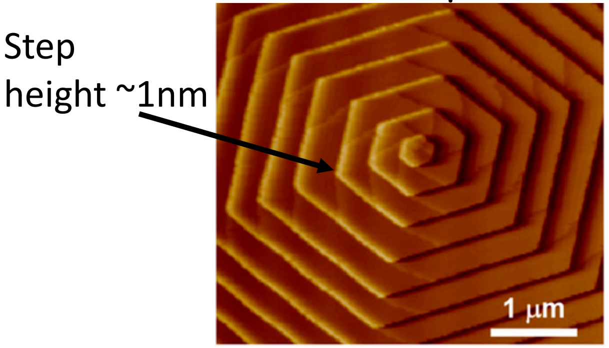
Thermal grooving in Ag (temp. T=920° C)



[Chalmers, King, Shuttleworth, 1948]

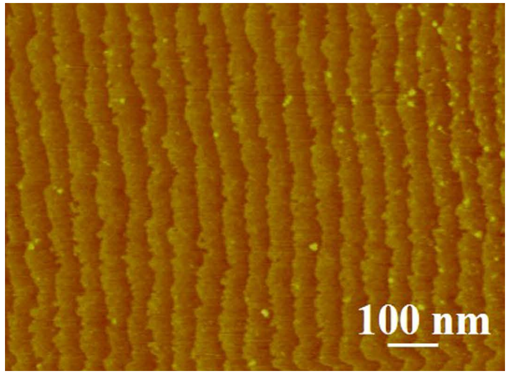
Goal: To model surface morphological evolution

Real-time observation of
L-cystine crystal growth in solution
(T close to room temperature)



[Shtukenberg, Zhu, An, Bhandari, Song, Kahr, Ward, 2013]

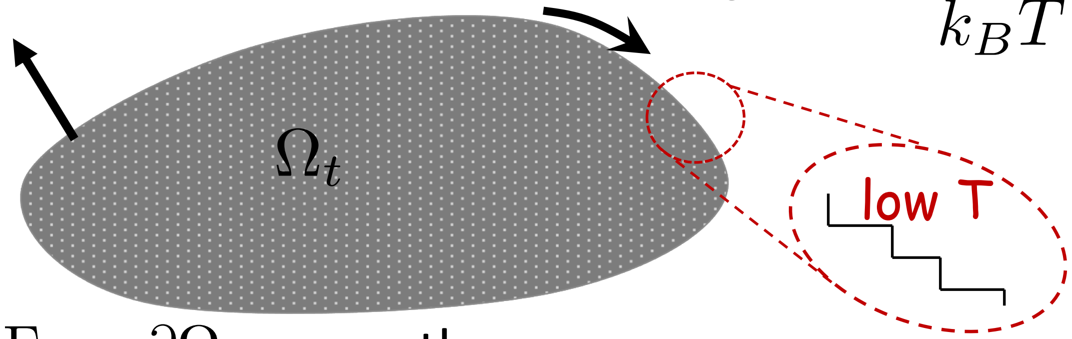
Atomic step formation on sapphire
surface (T close to room temp.)



[Wang, Guo, Xie, Pan, 2018]

"Classical" shape relaxation by surface diffusion

[Herring, 1950, 1951; Mullins, 1957]



surface flux

$$V_n = -\Omega \mathrm{div}_\Gamma \boldsymbol{J}$$

diffusivity, surface chem. potential

$$\boldsymbol{J} = -\frac{D_s \rho_{\mathrm{eq}}}{k_B T} \nabla_\Gamma \mu$$

(const.) surface free energy/area

$$\mu = \Omega \gamma \kappa$$

mean curvature

$\Gamma_t = \partial \Omega_t$: smooth

(Naive) Scaling prediction: $\tau \sim c(T) L^4$

lifetime, size

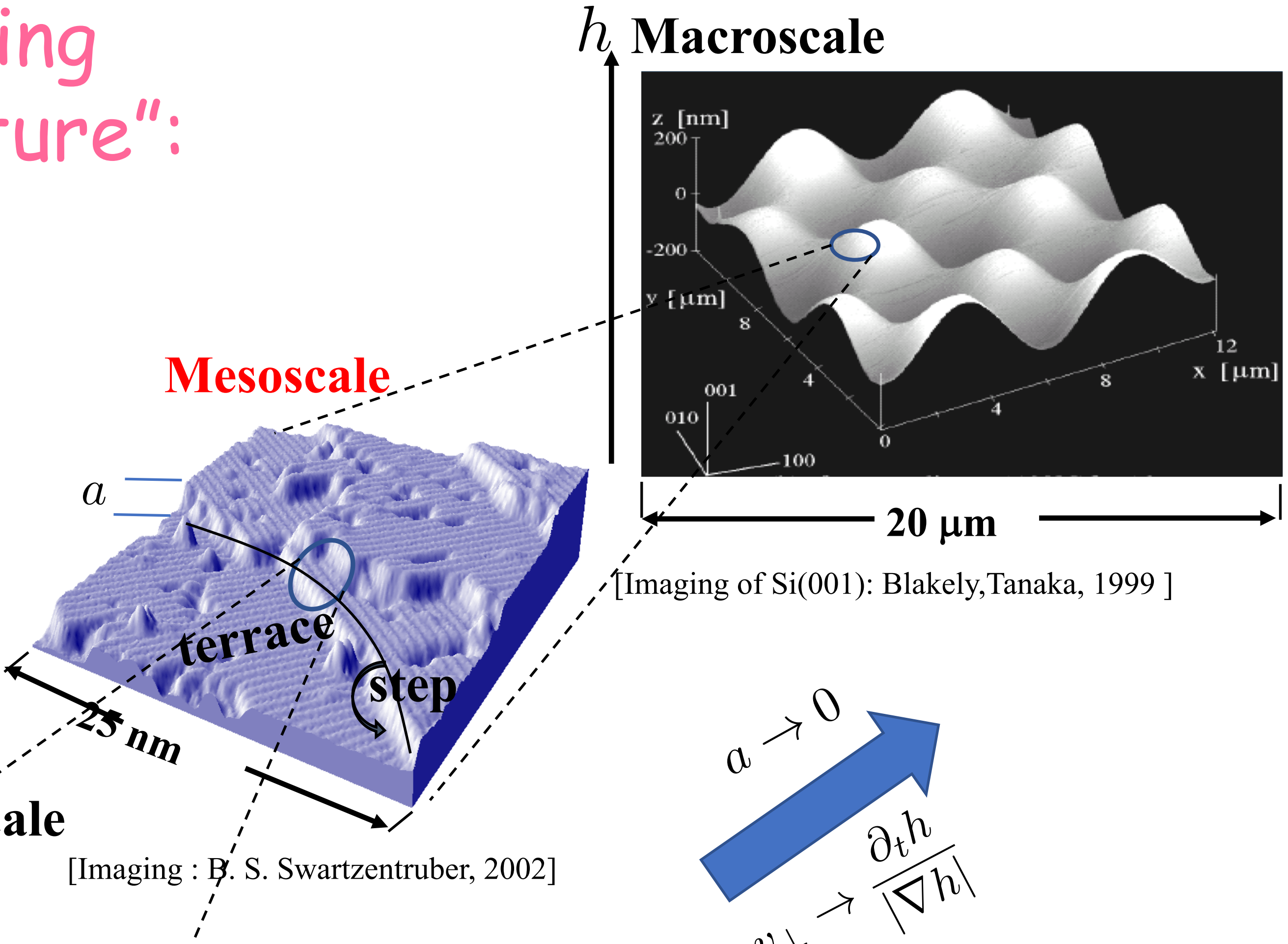
$$c(T) = CT/D_s(T)$$

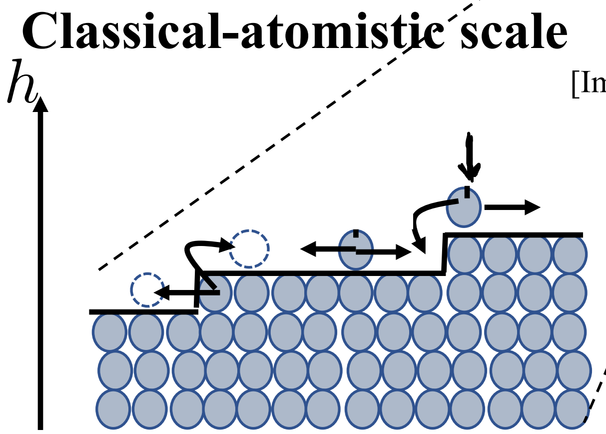
$$D_s(T) = D^0 e^{-E_a/(k_B T)}$$

Making smaller yet stable structures implies using lower temperatures.

[Gruber, Mullins, 1967; Rettori, Villain, 1988; Ozdemir, Zangwill, 1990 ...]

Below the "roughening transition temperature": Steps and terraces





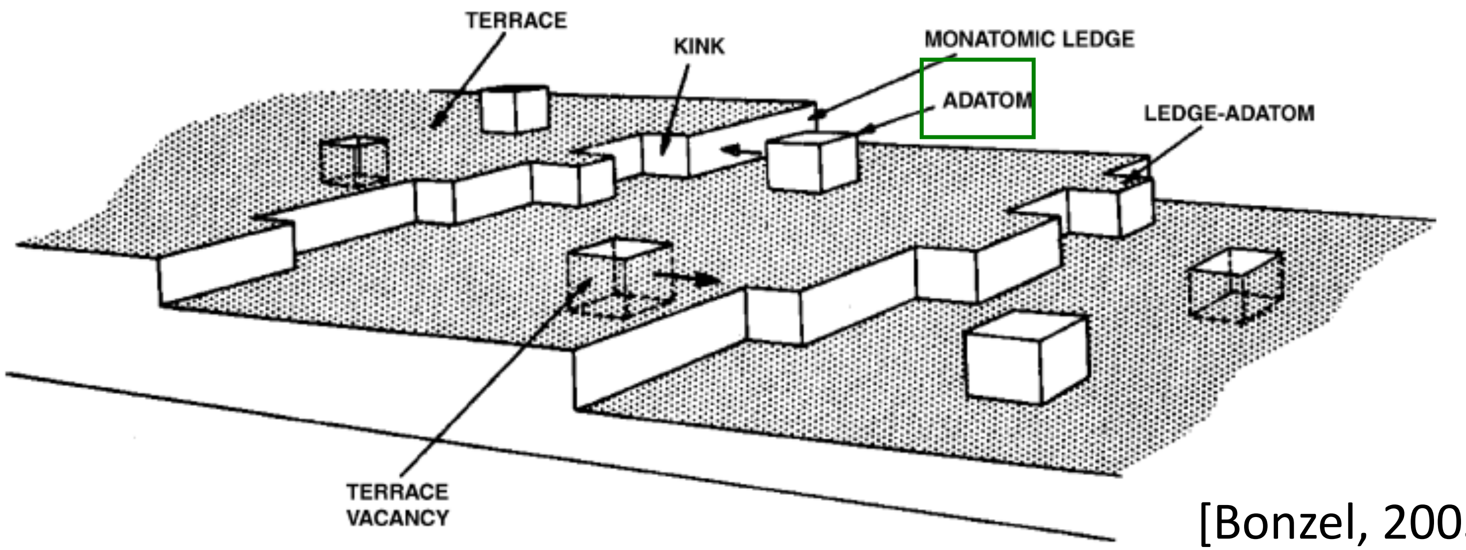
(Normal) Step velocity

How can one reconcile models across these scales?
What is a suitable macroscale description?

Defects on elemental cubic (Kossel) crystal

[Kossel, 1927; Stranski, 1928]

Idealized surface of cubic elemental crystal. Adsorbed atoms: “adatoms”.
Prominent microstructural features: terraces, steps (ledges), kinks.



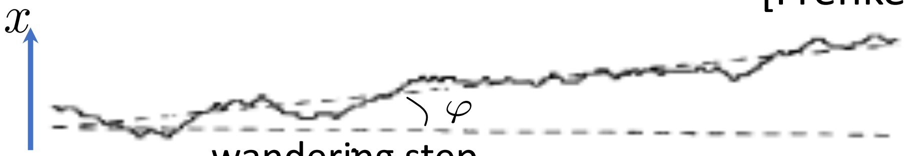
[Bonzel, 2003]

Surface evolution: Burton, Cabrera and Frank (BCF) model, 1951.
We need some equilibrium concepts.

Equilibrium Concepts: A Review

Roughening transition temperature: Single step

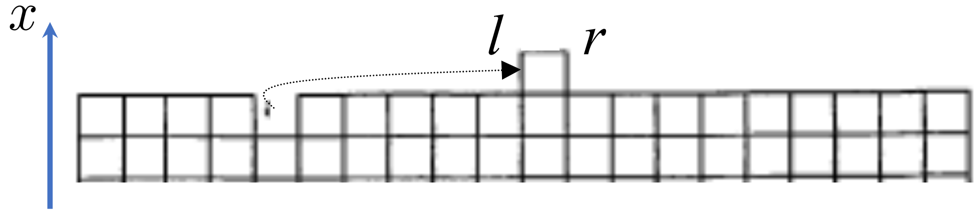
[Frenkel, 1945; Jayaprakash, Rottman, Saam, 1984; Zangwill, 1988; Saito, 1996; Tsao, 1993]



Surfaces contain *steps* : energetics include *kink* excitations.

Tendencies:

- Entropy increase due to kink-induced step wandering
- Step energy decrease since kinks cost energy



Key assumptions:

Isolated step.

Kinks cause step motion by 1 lattice site.

Toy model:

Probabilities p_l (left-facing kinks), p_r (right-facing kinks), p_0 (no kinks):

step free energy; energy; entropy; energy of straight step

$$f_{st} = u_{st} - T s_{st} = \mathcal{E}_{st} + (p_l + p_r)\mathcal{E}_{kink} + k_B T(p_l \ln p_l + p_r \ln p_r + p_0 \ln p_0)$$

$$p_l + p_r + p_0 = 1,\ \ p_l - p_r = \underbrace{\tan\phi}_{\text{fixed}} =: p_{ex};\ \ p_{in} := p_l + p_r - p_{ex} = 2p_r$$

Equilibrium:

Minimize f_{st} with respect to p_{in} for fixed ϕ and T.

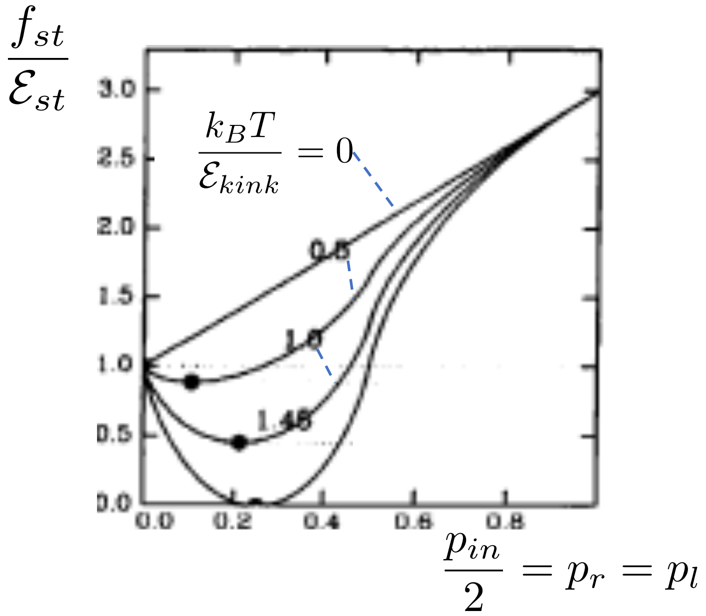
$$\text{Let}\quad f_{st}^{\text{eq}} := \min_{p_{in}}\{f_{st}\,|\,\text{fixed } \phi, \text{ fixed } T\}$$

Roughening transition temperature, $T_{R,st}$: $\quad f_{st}^{\text{eq}} = 0 \quad \text{at } T = T_{R,st}$

Roughening transition temperature: Steps (cont.)

[Saito, 1996; Tsao, 1993; Jeong, Williams, 1999]

$\phi = 0,\ \mathcal{E}_{st} = 2\mathcal{E}_{kink}$:



Crude approximation; e.g.,
by neglect of step interactions, noncrossing.

More advanced treatments account for: kinks moving steps by more than 1 lattice unit; step noncrossing.

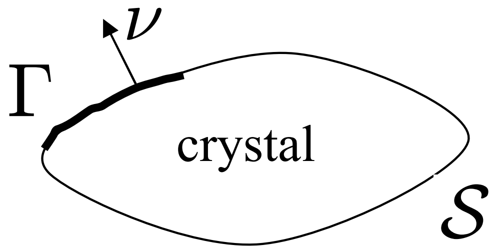
These are based on analogy between noncrossing steps & 1D spinless Fermion gases (Pauli exclusion principle).

[Jayaprakash, Rottman, Saam, 1984; Kosterlitz, Thouless, 1973; Schulz, 1985]

Mean field approaches are known to offer incomplete understanding; fluctuations are important.

[Jackson, 1975; Chui, Weeks, 1976; Nozieres, Gallet, 1987…]

Continuum surface free energy



Free energy of surface $\Gamma \subset \mathcal{S}$

$$E[\Gamma] = \int_\Gamma \gamma(\nu)\, dA = \int_{\tilde{\Gamma}} \tilde{\gamma}(\nabla h)\, dx dy \qquad h = h(x,y) : \text{graph (height)}$$

free energy per projected area

- $T > T_R$: smooth $\tilde{\gamma}(p)$ [Herring, 1950; Mullins, 1957, 1959]

- $T < T_R$: singular $\tilde{\gamma}(p)$ [Gruber, Mullins, 1967; Jayaprakash, Rottman, Saam, 1984]

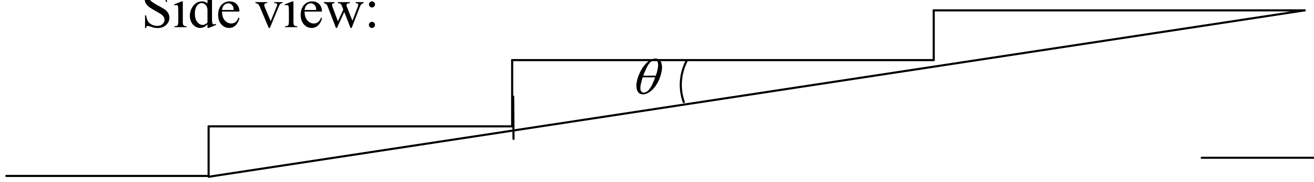
positive slope or step density, $\tan\theta$

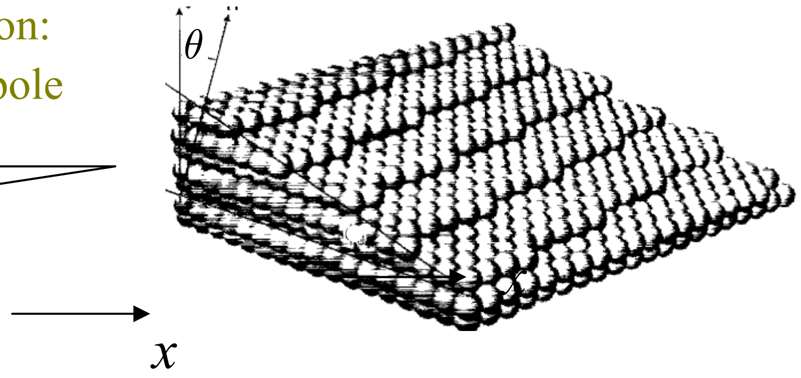
$$\tilde{\gamma}(p) = g_1|p| + \frac{g_3}{3}|p|^3 = \left(g_1 + \frac{g_3}{3}p^2\right)|p|\,, \quad g_{1,3} > 0; \qquad \text{continuum: } p = \partial_x h$$

step energy (line tension)

step-step interaction: entropic, elastic-dipole

Side view:





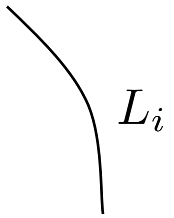
Discrete surface energy and limit, $T<T_R$: Heuristics

[DM, Kohn, 2006]

$$E_N^{st} = \sum_{i=1}^{N} a \int_{L_i} ds \; (g_1 + V_{i,i+1})$$

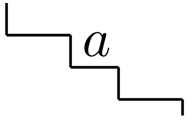
step line tension

Entropic & elastic-dipole nearest-neighbor step-step interactions



(step as smooth curve)

Continuum limit: $a \to 0$, fixed surface slope



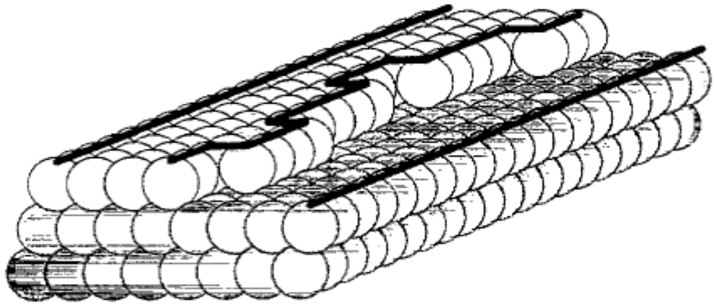
$$\sum_i a \to \int dh \;; \qquad \text{Coarea formula: } \int dh \int ds \,\cdot = \int\!\!\int dx\, dy\, |\nabla h| \,\cdot$$

$$E_N^{st} \to E[h]$$

Usually convex

Entropic step-step repulsions

[Gruber, Mullins, 1967; Jayaprakash, Rottman, Saam, 1984; Saito, 1996; Jeong, Williams, 1999]



$2w$

- Gruber and Mullins considered step wandering via kink formation.

Wandering is constrained: step does *not pass* neighboring steps (to first approximation, neighb. steps are treated as straight walls)

Step configurational entropy between walls of separation $2w$:

$$S(w;T) = S_0(T) - \tilde{g}(T)/w^2$$

- Same behavior if walls are replaced by neighb. steps; $w \longrightarrow a/|\tan\theta|$

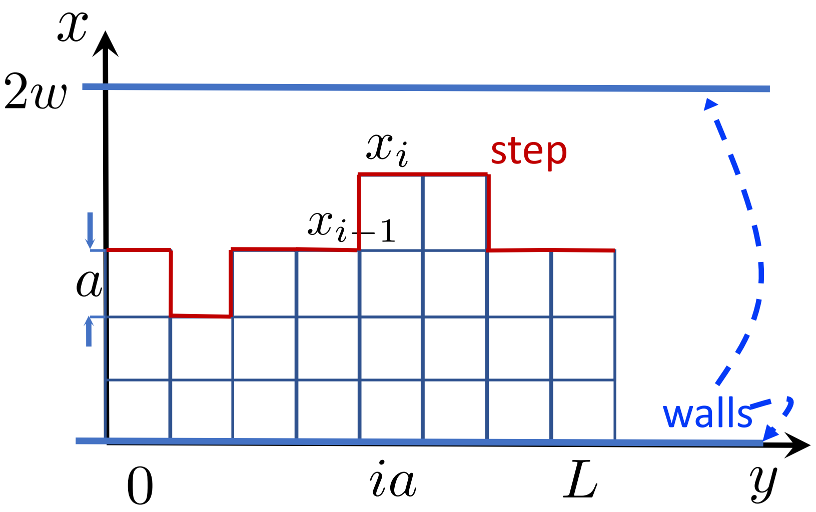
$$\tilde{\gamma}(\tan\theta;T) = g_0(T) + [\overbrace{(f_0 - TS_0)/a}^{g_1}]|\tan\theta| + [\overbrace{T\tilde{g}(T)/a^3}^{g_3/3}]|\tan\theta|^3$$

free energy cost per isolated step

[Jayaprakash, Rottman, Saam, 1984]

Entropic step-step repulsion: Sketch of calculation

[Gruber, Mullins, 1967; Saito, 1996]



Energy of system (model Hamiltonian):

$$\mathcal{H}(\{x_i\}_{i=1}^{L/a}) = \mathcal{H}_0 + J \sum_{i=1}^{L/a} \frac{|x_i - x_{i-1}|}{a}$$

due to kink formation

$$x_i/a = 1, \ldots, \frac{2w-a}{a}$$

Partition function:

$$Z = \sum_{\frac{x_1}{a}=1}^{(2w-a)/a} \cdots \sum_{\frac{x_N}{a}=1}^{(2w-a)/a} e^{-\mathcal{H}(\{x_i\})/(k_B T)} = e^{-\mathcal{H}_0/(k_B T)} \mathrm{tr}\left[\boldsymbol{T}^N\right]$$

$(N = L/a \gg 1)$

$\frac{(2w-a)}{a} \times \frac{(2w-a)}{a}$ tri-diagonal, pos. symmetric matrix depending on $e^{-J/(k_B T)}$

$$\mathrm{tr}\left[\boldsymbol{T}^N\right] = \sum_{k=1}^{(2w-a)/a} \lambda_k^N \approx \lambda_1^N \qquad (\lambda_{k-1} > \lambda_k;\ \text{all } k);\ \lambda_k:\ \text{eigenvalues of } \boldsymbol{T}$$

$$\lambda_k = 1 + 2e^{-J/(k_B T)} \cos\left(\frac{\pi k}{2}\frac{a}{w}\right)\ ;\ |\tan\theta| = \frac{a}{w}$$

Step free energy (per unit step length):

$$\beta(\theta) = -\frac{k_B T \ln Z}{L} \approx \frac{\mathcal{H}_0}{L} - \frac{k_B T}{a} \ln \lambda_1 \approx \beta_0 + \beta_2 (\tan\theta)^2$$

Step-step elastic-dipole interactions

Elastic properties of crystal surfaces

V. I. Marchenko and A. Ya. Parshin

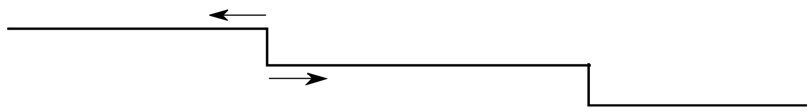
S. I. Vavilov Institute of Physics Problems, Academy of Sciences of the USSR, Moscow
(Submitted 11 January 1980)
Zh. Eksp. Teor. Fiz. **79**, 257–260 (July 1980)

The general properties of the surface stress tensor, describing elastic properties of crystal surfaces, are determined. The boundary conditions are obtained for the bulk stress tensor on the surface of a crystal of arbitrary shape. The elastic interaction between point and line defects on crystal surfaces is considered.

PACS numbers: 68.25. + j, 61.70.Yq

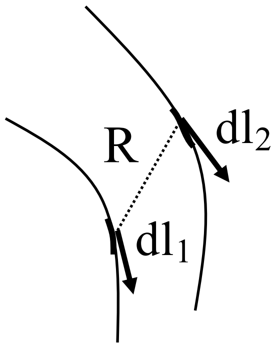
It is well known that the thermodynamic properties of a liquid surface are governed entirely by one quantity which is the work done in reversible changes of the surface area. As pointed out long ago by Gibbs,[1] in the case of a solid we have to distinguish the work done in forming the surface and in deforming it. Thus, in describing the properties of crystal surfaces we have to introduce not only the surface energy but also the surface stress tensor. We shall determine the general properties of this tensor and find the boundary conditions replacing in our case the familiar Laplace formula for the capillary pressure.

In the second section we shall consider the elastic interaction of surface defects over distances which are large with the atomic separations. As in the case of



Each step is modeled as a force dipole.
Dominant dipole moment is along step edge, parallel to terrace.

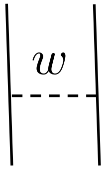
[For a thorough exposition, see book by Pimpinelli & Villain, 1998]



Elastic-dipole interaction energy of infinitesimal step segments 1 and 2:

$$d^2E_{12} \propto \frac{d\mathbf{l}_1 \cdot d\mathbf{l}_2}{R^3}$$

Interaction energy *per unit length* for straight step: $\frac{dE_{int}}{dl} \propto w^{-2}$



Continuum limit: Energy density $\propto |\tan\theta|^2 |\tan\theta|$

Digression: On the missing p^2 term $(T<T_R)$

$$\tilde{\gamma}(p) = g_1|p| + \frac{g_2}{2}p^2 + \frac{g_3}{3}|p|^3 \ ; \qquad p = \nabla h \ .$$

Against p^2 term :

- Direct derivation of $\tilde{\gamma}$ for entropic or elastic-dipole step-step interactions [Gruber, Mullins, 1967; Jayaprakash, Rottman, Saam, 1984].
- Experimental evidence: equilibrium Pb crystal shapes [Bonzel, 2003]
- Some DFT computations on Pb surface [Yu, Bonzel, Scheffler, 2006]
- Theoretical argument by *reductio ad absurdum* for specific 1D geometry [Najafabadi, Srolovitz, 1994] .

However…

- García and Serena [1995] link p^2 term to *electronic surface states.*

However: Another calculation gives term $|p|^{5/2}\sin(q_F a/|p| + \theta_0)$, q_F: Fermi wavenumber [Hyldgaard, Einstein, 2005; DM, Bonzel, Scheffler, *unpub.*]
Strong quantum coherence is required (difficult at $T > 0$)

- *Special* networks of crossing steps [Carlon, van Beijeren, 1996; Vilfan, 1996]
- *Special* case of local strain on Si(001) [Swartzentruber *et al.*, 1993]

Equilibrium crystal shape

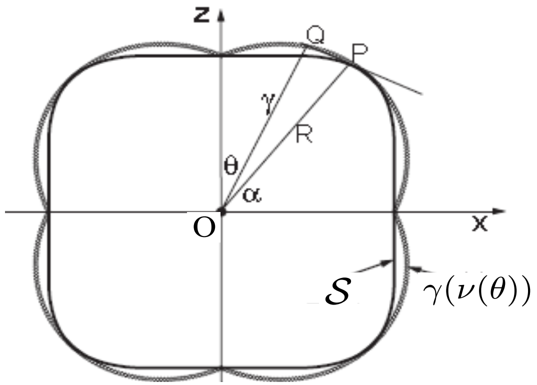
[Wulff, 1901; Hilton, 1903; Herring, 1951; Landau, Lifshitz, 1958; Taylor, 1974; Andreev, 1982]

Wulff problem: Given $\gamma(\nu)$, find the crystal shape $\mathcal{S}$ that **minimizes** $E[\mathcal{S}]$ for fixed volume enclosed by $\mathcal{S}$

Wulff construction: The crystal shape $R(\alpha)$ or $z(x)$ satisfying the Wulff problem is formed by the *inner envelope* of hyperplanes normal to radial vector of polar plot (r, θ, ϕ) of γ; $r = \gamma$, (θ, ϕ): angular coordinates of ν

Example: 1D case of vicinal surface [Bonzel, 2003]:

1D aspect: Normal vector to Wulff shape is *time self-similar solution* of an associated Riemann problem for hyperbolic conservation law [Peng, Osher, Merriman, Zhao, 1999]

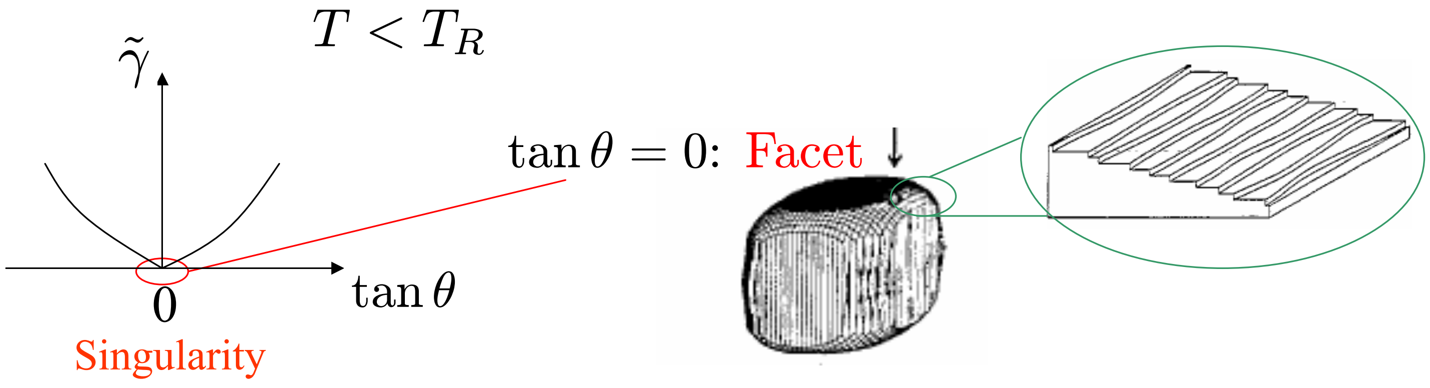


Legendre transform ("Andreev construction") In 1D, the equilibrium crystal shape is the *Legendre transform* of the projected free energy density, $\tilde{\gamma} = \gamma/\cos\theta$, in the variable $m = \tan\theta$. This can be extended to 2D. For approp. cont. differentiable $\tilde{\gamma}$, the shape is described by $x \mapsto z$ where

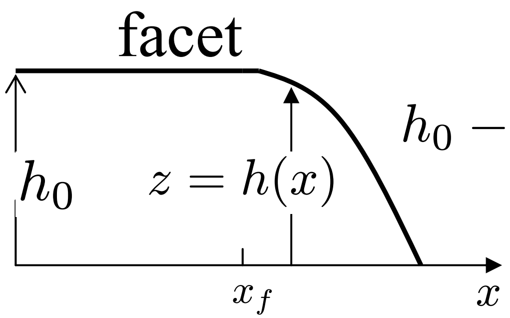
$$x = \frac{1}{ß}\frac{\partial\tilde{\gamma}}{\partial m}, \quad z = \frac{1}{ß}\left(\tilde{\gamma} - m\,\frac{\partial\tilde{\gamma}}{\partial m}\right); \; ß : \text{Lagrange mult.}$$

Facets from a continuum view

Below the roughening temperature, T_R, (corner) singularities of $\tilde{\gamma}$, as a function of slope $m = \tan\theta$, correspond to planar macroscopic surface regions of the equilibrium crystal shapes, called **facets**.



1D: By Legendre transform of $\tilde{\gamma}(p) = g_1|p| + (g_3/3)|p|^3$,



$$h_0 - h(x) = \frac{2}{3}\left(\frac{\beta}{g_3}\right)^{1/2}(x - x_f)^{3/2} + \mathcal{O}((x - x_f)^2) \quad x \to x_f$$

[Jayaprakash, Saam,1984; Rottman,Wortis,1984]

Good agreement with experimental data for Pb crystallites [Bonzel,2003]

Surface Motion near Equilibrium:

An Introduction

Remarks on crystal surface motion

- Early theories of crystal surfaces invoke concepts of continuum thermodynamics.
- Advantage: direct use of large scales.
- Disadvantage: Below the roughening transition temp., the relation of steps to continuum is tricky.

One of our goals is to illuminate connection of full continuum (PDEs for surface height) to step motion (BCF model).

Lecture II

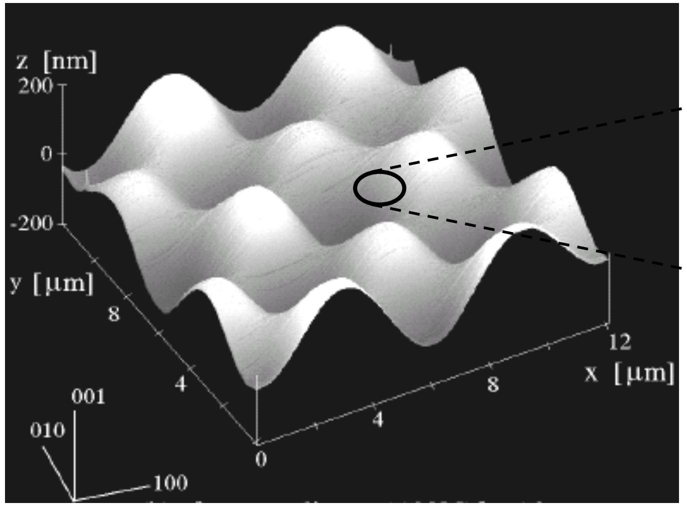
By use of a 1D model for the random motion of individual atoms, we will heuristically show the **plausible emergence** of a simplified BCF-type model (in 1+1 dimensions).

Lecture III

$T<T_R$: Two scales and their relation

h

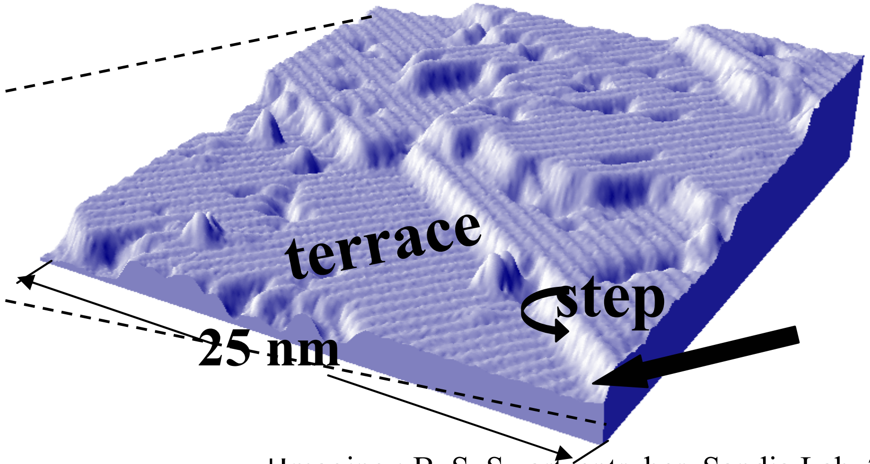
``**Macroscale**''; scale λ



20 μm

[Imaging of Si(001): Blakely,Tanaka, 1999]

Nanoscale [same material/orientation]



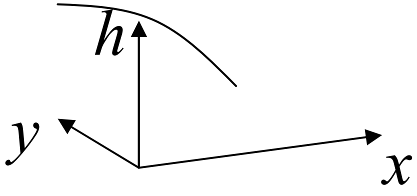
~1 atom; height a

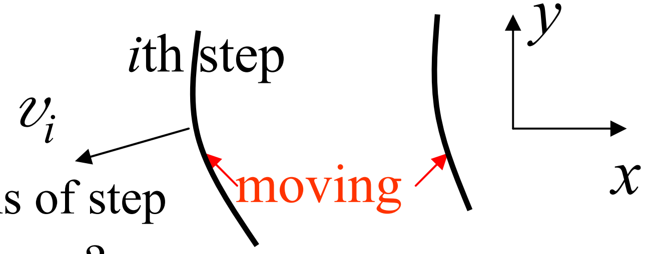
[Imaging : B. S. Swartzentruber, Sandia Lab, 2002]

Steps modeled by *smooth curves* [BCF, 1951]

Motion of ***steps***: ***Discrete scheme***

PDE for height h

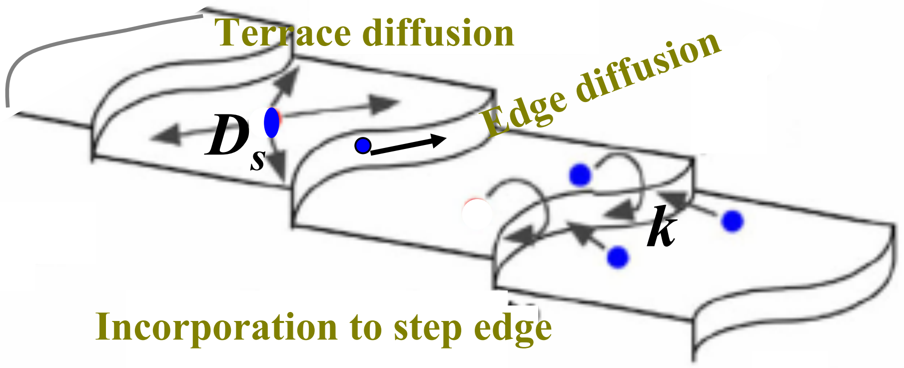




: In terms of step positions ?

Microscopic processes

[**B**urton, **C**abrera, **F**rank, 1951]



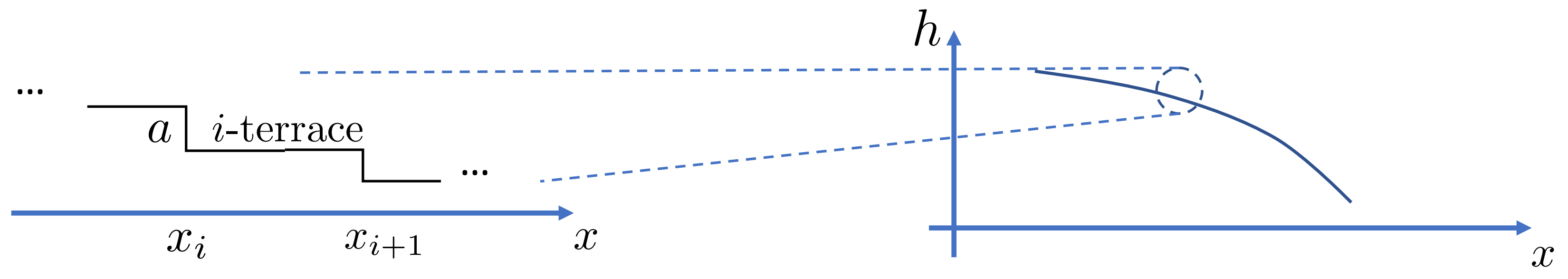
(Asymmetrically with
ES=Ehrlich-Schwoebel barrier;
rates k_u & k_l)

Steps move by mass conservation as atoms attach/detach at them.

Combination of thermodynamic and kinetic effects.

Step motion and continuum limit (heuristics): Example in 1D

[Nozieres, 1987; Rettori, Villain, 1988; Ozdemir, Zangwil, 1990]



Step velocity

Mass flux on i-th terrace

$$\dot{x}_i = a(J_{i-1} - J_i) \qquad \text{at } x = x_i$$

$a \to 0$

$$\partial_{\tilde{t}} h = -\partial_x J$$

Mass conservation

Diffusion; Attachment/detachment

$$\begin{cases} -J_i = q(\rho_i - \rho_i^{\text{eq}}) & \text{at } x = x_i^+ \\ J_i = q(\rho_i - \rho_{i+1}^{\text{eq}}) & \text{at } x = x_{i+1}^- \end{cases}$$

(i-th terrace)

Adatom density

$$D_s \partial_{xx} \rho_i = \partial_t \rho_i \approx 0 \, , \quad J_i = -D_s \partial_x \rho_i \quad x_i < x < x_{i+1}$$

$$J = -\frac{D_s}{1 + \frac{D_s}{qa}|\nabla h|} \partial_x \rho^{\text{eq}}$$

Diffusion-limited kinetics

"Fick's law" for surface diffusion

Step chemical potential, near equilibrium

Gibbs-Thomson rel.

$$\rho_i^{\text{eq}} = \rho_s e^{\mu_i / T}$$

step chem. potential

Total step energy (N steps)

$$\mu_i = a \frac{\delta E_N^{\text{st}}}{\delta x_i}$$

$$\rho^{\text{eq}} = \rho_s e^{\mu / T}$$

$$\mu = a \frac{\delta E[h]}{\delta h}$$

Near-equilibrium condition

On coarse graining of step motion (heuristics)

- Step density is assumed to vary slowly across terraces.
- Formally, discrete variables are expanded in Taylor series, e.g.,

$$X_j \approx \mathcal{X}(\underbrace{j\overset{a}{\epsilon}}_{h}) \; : \; X_{j+n} \approx \mathcal{X}(h) + (n\epsilon)\mathcal{X}_h(h) + \frac{1}{2}(n\epsilon)^2\mathcal{X}_{hh} + \dots \quad \text{as } \epsilon \to 0$$

- More careful treatment invokes weak formulation [DM, Kohn, 2006]
- In 2D, the continuum-scale surface mobility emerges from step flow kinetics as a 2nd-rank tensor [DM, Kohn, 2006]. **No** 1D analog (see Lecture II)

This approach becomes questionable, when, e.g.

- Coarse graining occurs near **facets** (Lecture II)
- Parameters vary from one terrace to the next, e.g., in surface reconstructions.

Continuum surface energy & typical relaxation by surface diffusion

For surface relaxation (without ext. deposition) in Diffusion-Limited regime, PDE for height, *h*, is:

$$\frac{\partial h}{\partial t} = \Delta \left(\frac{\delta E}{\delta h} \right)_{L^2}$$

$$E[h] = \int g_1 |\nabla h| + \frac{g_3}{3} |\nabla h|^3 \, dx$$

Outside facets.
Structure is consistent with (discrete) step flow

This structure admits extensions; **surprises in regard to kinetic mobility** (Lecture II)

Including facets: *Fully continuum framework*:

$$\frac{\partial h}{\partial t} \in -\partial_{H^{-1}} E$$

(subdifferential of E)

``Extended-gradient formalism"

[Kobayashi, Giga, 1999; Spohn, 1993; Odisharia, Thesis, 2006; Kashima, 2004; Giga, Giga, 2010; Giga, Kohn, 2011]

Flavor of abstract framework: Extended-gradient formalism

Evolution PDE is everywhere replaced by the rule that $-\partial_t h$ is an element of subdifferential $\partial_{\mathcal{H}} E[h]$ with minimal norm in Hilbert space $\mathcal{H}$.

$$\partial_{\mathcal{H}} E[h] := \{f \in \mathcal{H} \,:\, E[h+g] - E[h] \geq (f,g)_{\mathcal{H}} \quad \forall g \in \mathcal{H}\}$$

Typically: $\mathcal{H} = L^2$, H^{-1}

reflects kinetics

evaporation

surface diffusion: DL kinetics

"Natural" boundary conditions at facet edges follow.

What should the above rule amount to, practically?

Suppose the facet is smoothed out via regularization of $E[h]$ by some parameter, ν. Then, in the limit as ν approaches 0, one should recover the evolution of the above formalism.

Digression: ODE (toy) model

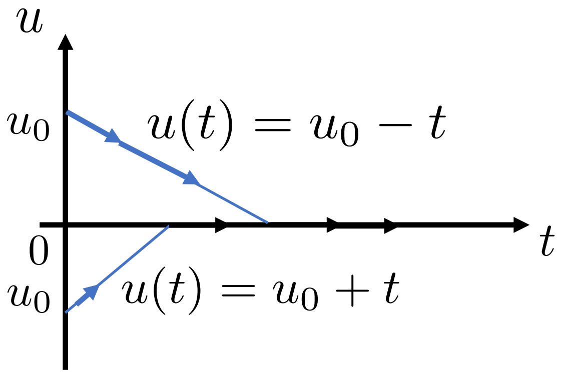
[Kobayashi, Giga, 1999]

Find the continuous solution to ODE:

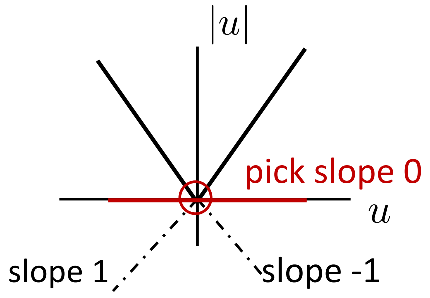
$$\frac{u(t)}{|u(t)|} = \left(\frac{\delta}{\delta u}\right)|u| \text{ if } u \neq 0$$

$$\frac{\mathrm{d}u(t)}{\mathrm{d}t} = -\mathrm{sgn}(u(t))\,; \quad u(0) = u_0$$

(What happens if $u = 0$?)



Define $\frac{\mathrm{d}u}{\mathrm{d}t} = 0 \text{ if } u = 0$



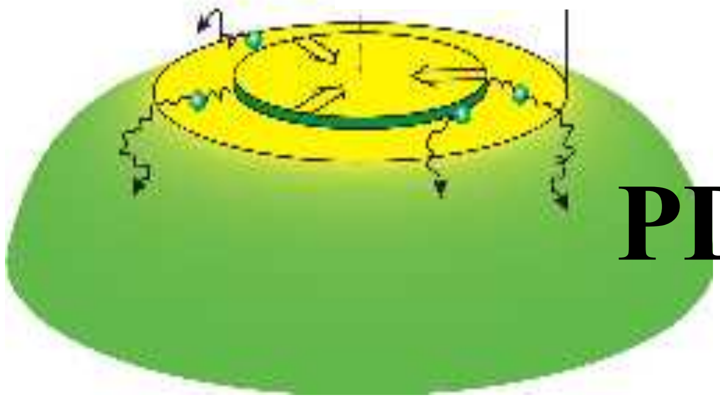
"Extended-gradient formalism"

$$\Rightarrow u(t) = \begin{cases} u_0 - t\,\mathrm{sgn}(u_0)\,, & 0 \leq t \leq |u_0| \\ 0\,, & t > |u_0| \end{cases}$$

This result can be recovered by regularization, e.g., consider

$$\frac{\mathrm{d}u^\epsilon(t)}{\mathrm{d}t} = -\frac{u^\epsilon(t)}{\sqrt{u(t)^2 + \epsilon^2}}\,; \text{ small } \epsilon \ (\epsilon \downarrow 0)$$

Subgradient formulation is in principle
not consistent with step flow



PDE

Microstructure on top of facets matters (Lecture II)

[Israeli, Kandel, 1999; DM, Fok, Aziz, Stone, 2006; Nakamura, DM, 2013; Schneider, Nakamura, DM, 2014]

Our understanding so far relies on specific examples

Epilogue: The regime below roughening transition

- Step motion is described by the BCF model [1951] and its extensions: near-equilibrium thermodynamics and kinetics of steps.

- PDEs for crystal surfaces must be viewed as **appropriate limits** of step flow. Dimensionality and kinetics affect the PDE structure crucially – see **Lecture II**.

- Issues for PDEs arise near facets, where microscale events influence continuum solutions; see **Lecture II**.

- Deviations from near-equilibrium kinetics can occur in actual materials. Extensions to **far-from-equilibrium** evolution of steps must account for motion of kinks. [Caflisch, E, Gyure, Merriman, Ratsch, 1999; Filimonov, Hervieu, 2004; Balykov, Voigt, 2005-6; Caflisch, Li, 2003; Kallunki, Krug, 2003; DM, Caflisch, 2008…]

- The BCF model, although mostly successful, is largely phenomenological. How does the BCF model **emerge** from atomistic dynamics? For a toy model in 1D, see **Lec. III**.