(Lecture I)

A tale of two scales: Fundamentals of crystal surface morphological evolution

Dionisios Margetis
Department of Mathematics, &
Institute for Physical Science and Technology, &
Ctr. for Scientific Computation and Mathematical Modeling
University of Maryland, College Park

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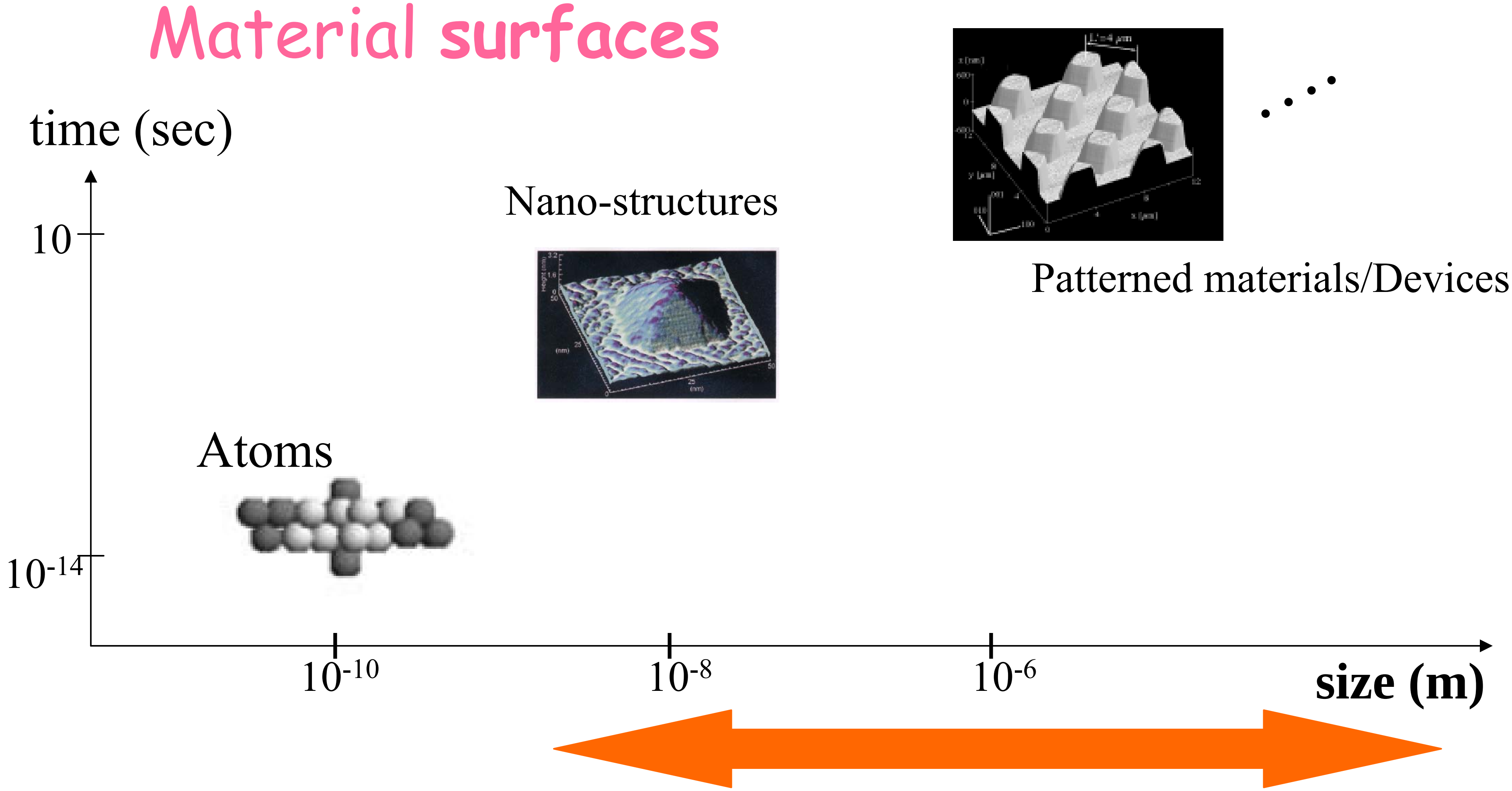
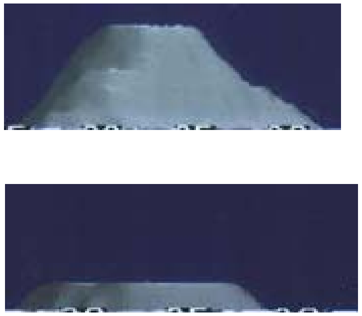
Material surfaces



Surface structures evolve, e.g., relax to become flat. Evolution laws?

Assumption: Motion near equilibrium



[Imaging on Si(111): Ichimiya, Tanaka, Hayashi, 1998]

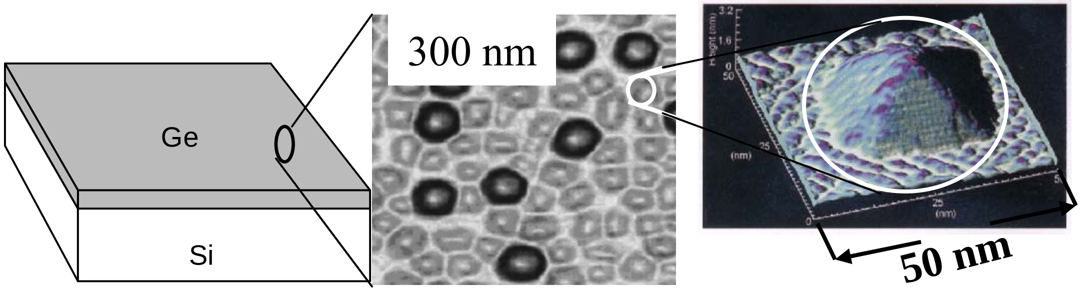
Motivation

- **Mathematics:** Studying relations of ***discrete schemes*** to macroscopic ***PDEs.*** Conventional interpretations of PDE are in principle **not** consistent with discrete schemes.

- **Materials science:** Designing desirable material behavior at macroscale by ***manipulation*** of smaller scales

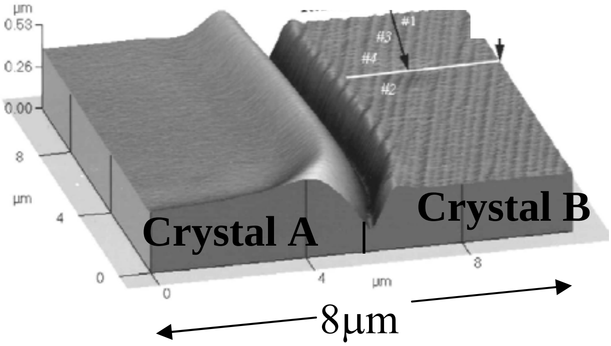
Applications (sample)

``Quantum-dot'' arrays for small devices



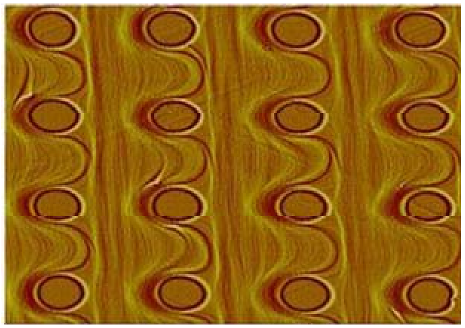
[Medeiros-Ribeiro *et al*., 1998]

Grain boundaries



[Sachenko *et al*., 2002]

Patterns on Si(111)



[Kwon *et al*, 2006]

Problem: Unpredictable surface morphology.

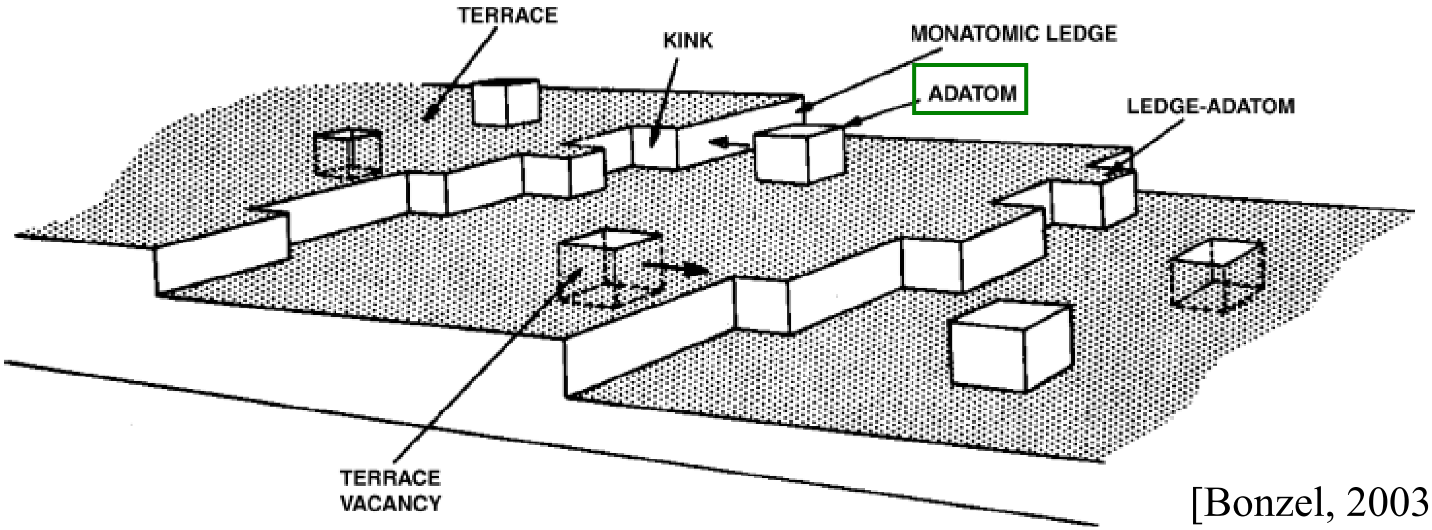
Mass transport path (example) on crystal surfaces:

Surface diffusion

Defects on elemental surface: Kossel crystal

[Kossel, 1927; Stranski, 1928]

Idealized surface of **cubic** elemental crystal
Prominent **microstructural** features: terraces, steps (ledges), kinks



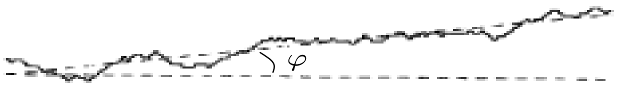
[Bonzel, 2003]

Surface **evolution**: Burton, Cabrera and Frank (**BCF**), 1951
Need some **equilibrium** concepts

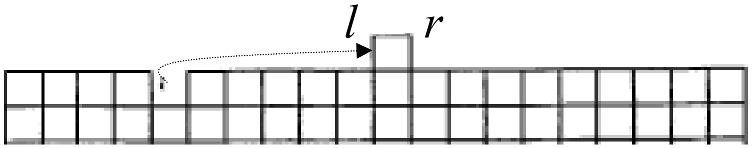
Equilibrium Aspects: A Review

Roughening temperature

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



wandering step



Surfaces contain *steps*: energetics include kink excitations

Competing tendencies:

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

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

$$\overset{\text{free energy}}{f_{st}} = \overset{\text{energy}}{u_{st}} - \overset{\text{entropy}}{T s_{st}} = \overset{\text{energy of straight step}}{\mathcal{E}_{st}} + (p_l + p_r)\mathcal{E}_{kink} + k_B T(p_l \ln p_l + p_r \ln p_r + p_0 \ln p_0)$$

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

Equilibrium $\boxed{f_{st} = \min_{p_{in}} f_{st}}$

Roughening temperature $T_{R,st}$: Condition on $\min f_{st}$ (at equilibrium):

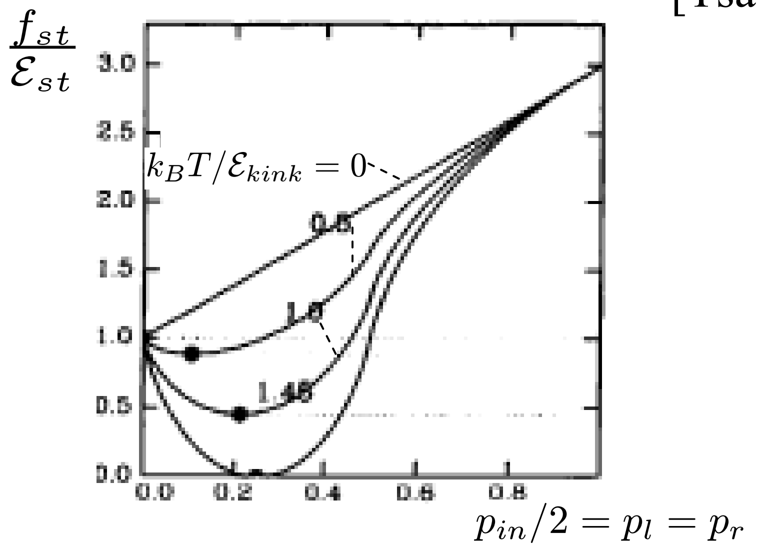
$$\min_{p_{in}} f_{st} = 0 \quad \text{at } T = T_{R,st}$$

If $T > T_{R,st}$, steps are created **spontaneously**

Roughening temperature: Steps (cont)

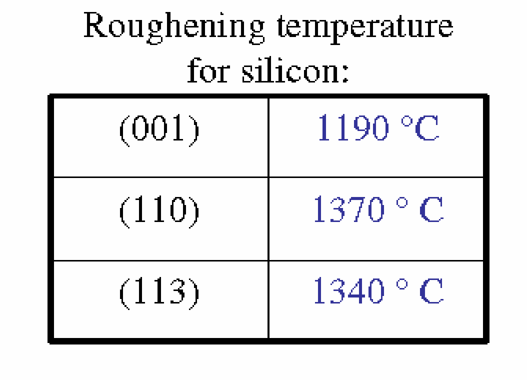
[Tsao, 1993; Jeong, Williams, 1999]

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



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

- For fixed material, $T_{R,st}$ depends on surface orientation



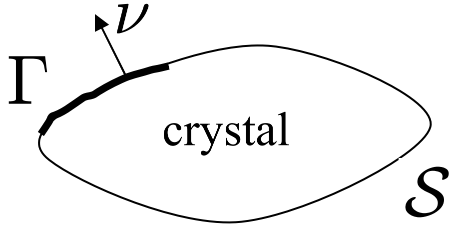
Roughening temperature
for silicon:

(001)	1190 °C
(110)	1370 ° C
(113)	1340 ° C

Words of caution

- Early theories for crystal surfaces invoke *continuum* thermodynamics
- Advantage: direct use at large scales
- Disadvantage: *Below roughening temperature*, *not clear* relation of continuum to steps.
- Our goal is to illuminate connection of full continuum to step motion (BCF model). Two scales of interest: nanoscale (steps) & macroscale.
- We do **not** address motion of individual atoms, e.g., Solid-on-Solid model and kinetic Monte Carlo algorithm details. In the same vein, we do **not** discuss the atomistic computation of material parameters.
- Stochastic effects are **not** discussed herein

Continuum surface energy



(Total) 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]

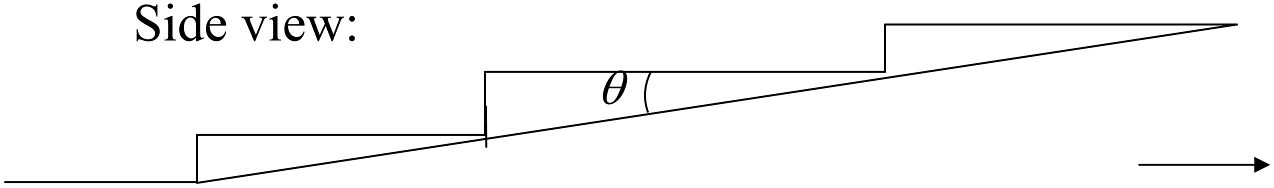
- $T < T_R$: singular $\tilde\gamma(p)$ [Gruber, Mullins, 1967; Jayaprakash, Rottman, Saam, 1984]

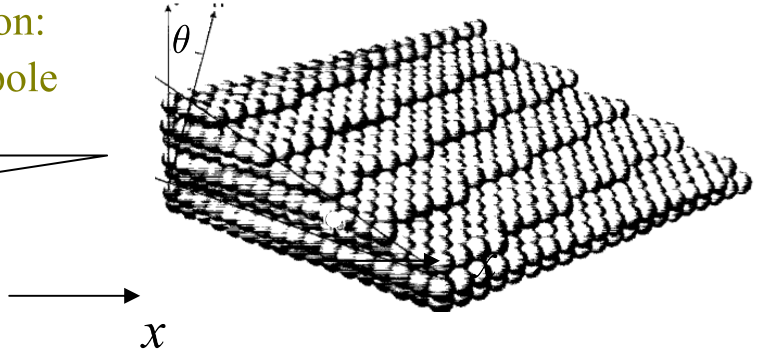
$$\tilde\gamma(p) = g_1|p| + \frac{g_3}{3}|p|^3 = \left(g_1 + \frac{g_3}{3}p^2\right)\overbrace{|p|}^{\substack{\text{positive slope or step density,}\\ \tan\theta}}, \quad g_{1,3} > 0; \qquad \text{continuum: } p = \partial_x h$$

step energy (line tension)

step-step interaction: entropic, elastic-dipole

Side view:





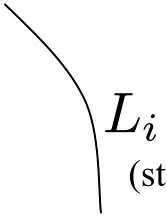
Discrete surface energy and limit: Formalities

[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-neighb. step interactions



(step as smooth curve)

Continuum; steps have same height, *a*: *a*→ 0

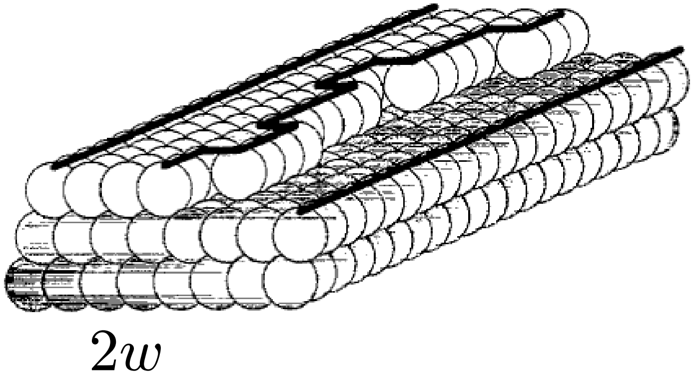
$$\sum_i a \longrightarrow \int dh \;; \qquad \text{coarea formula: } \int dh \int ds \,\cdot = \iint dx\, dy\, |\nabla h| \,\cdot$$

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

Usually convex

Entropic step-step repulsion

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



- 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 $2w$:

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

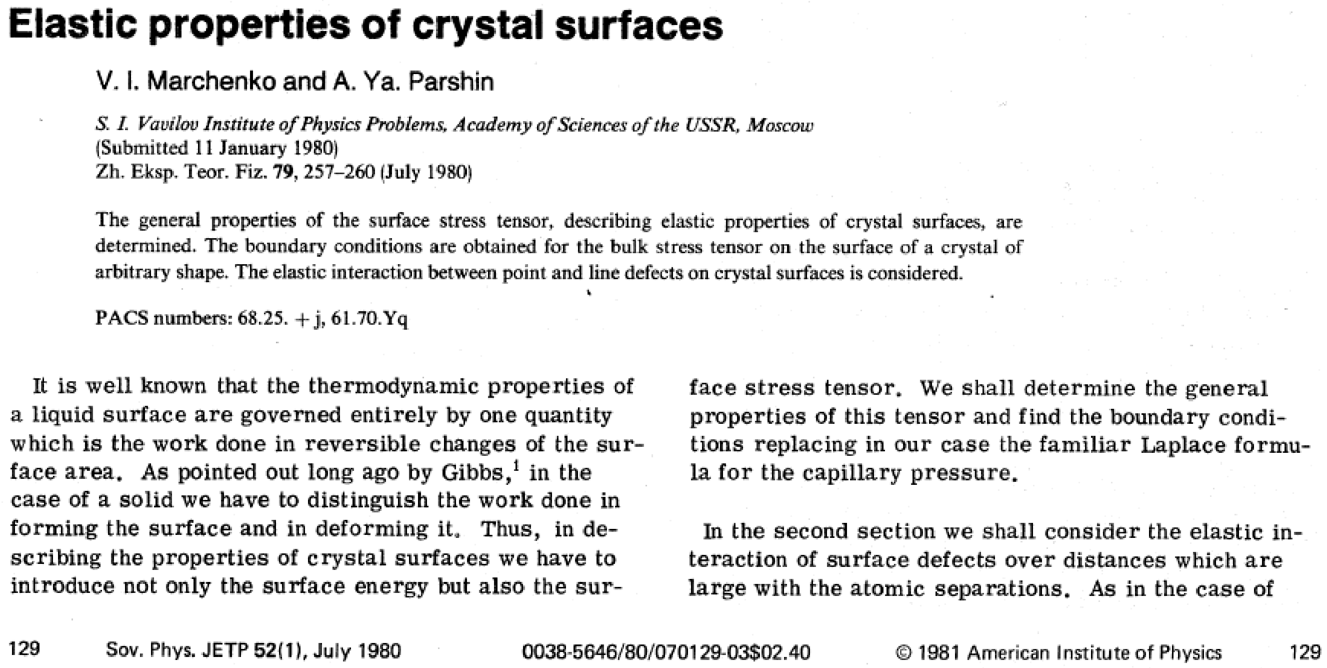
- Same behavior if walls are replaced by neighb. steps; $w \rightarrow a/|\tan\theta|$

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

free energy cost
per isolated step

[Jayaprakash, Rottman, Saam, 1984]

Step-step elastic-dipole interaction



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

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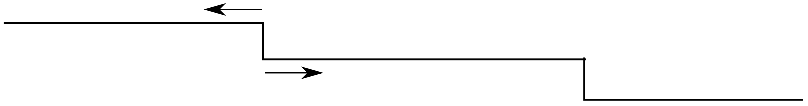
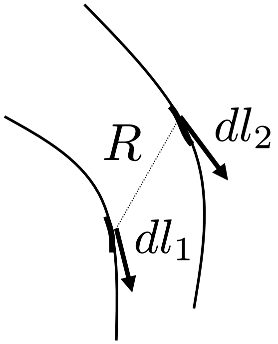


Each step is modeled as a force dipole.
Dominant dipole moment is along step edge, parallel to terrace

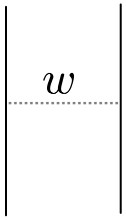
[See also Pimpinelli, Villain, 1998]



Elastic-dipole interaction energy of segments 1, 2:

$$d^2E_{12} \propto \frac{dl_1 \cdot dl_2}{R^3}$$

Energy *per unit length* for straight steps: $dE_{int}/dl \propto w^{-2}$



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

Other extensions: effects of stress [Kukta, Bhattacharya, 2002]

Diggression: On the missing p^2 term $(T<T_\mathrm{R})$

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

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 wavevector [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

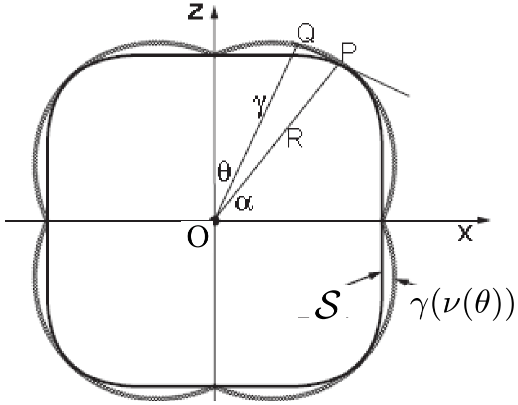
[Wulff, 1901; Hilton, 1903; Herring, 1951; Landau, Lifshitz, 1958; Taylor, 1974; Andreev, 1982]

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]



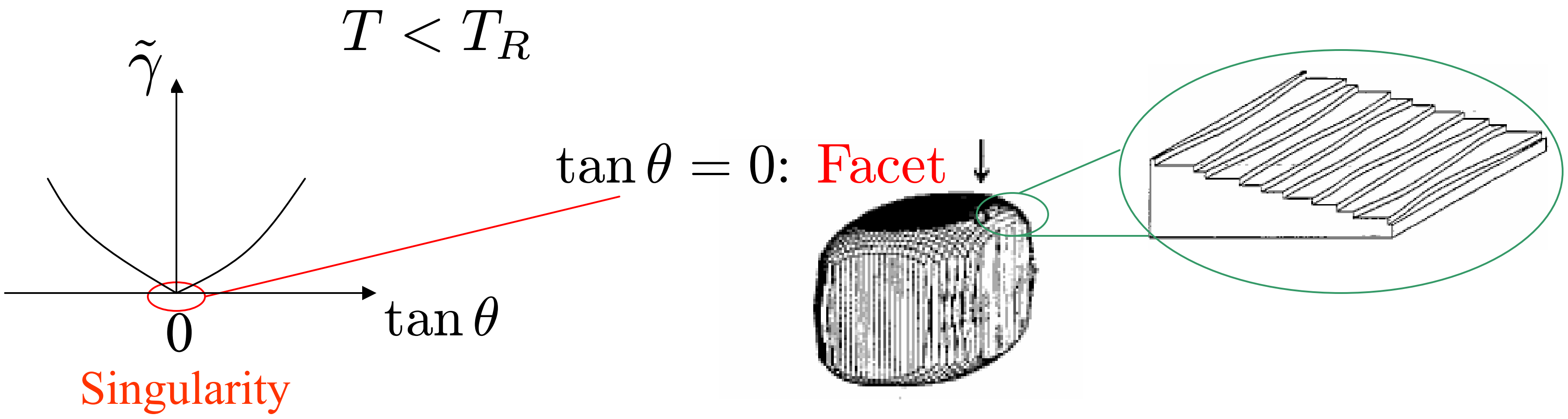
Legendre transform ("Andreev construction") In 1D, the equilibrium crystal shape is the *Legendre transform* of the projected free energy density, $\tilde\gamma = \gamma/\cos\theta$, in the variable $m = \tan\theta$. This can be extended to 2D. For approp. cont. differentiable $\tilde\gamma$, the shape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

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

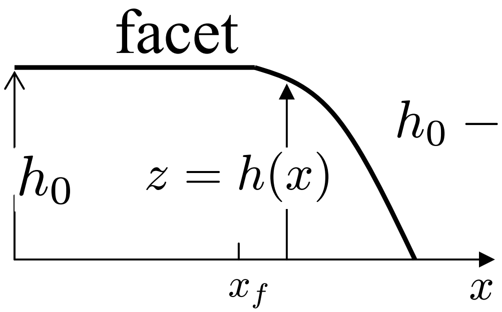
Facets (thermodynamically)

- Below 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 shape, called **facets**

[Jeong, Williams, 1999]



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



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

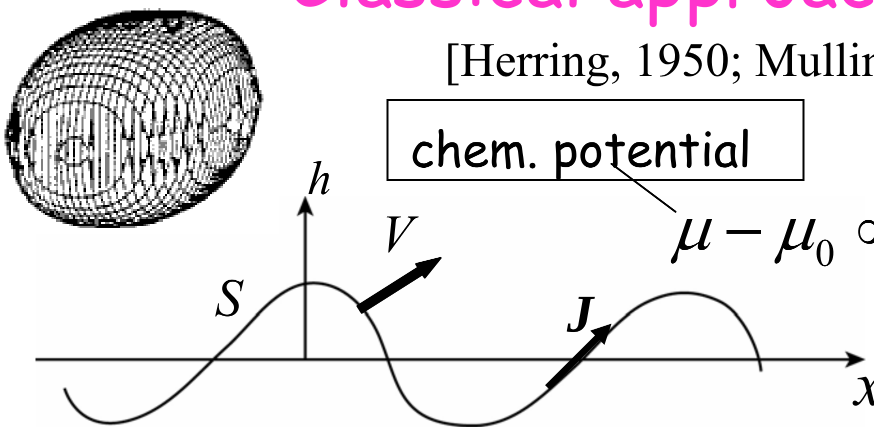
[Jayaprakash, Saam,1984; Rottman,Wortis,1984]

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

Surface Motion near Equilibrium: An Introduction

Classical approach to relaxation, $T > T_{\mathrm{R}}$

[Herring, 1950; Mullins, 1957, 1959; Cahn, Taylor,1994]



chem. potential

$$\mu - \mu_0 \propto \kappa^{(S)}$$

mean curvature

$$\begin{cases} \mu - \mu_0 = \dfrac{\delta E}{\delta h} \\ E[h] = (1/2)\displaystyle\int dx\,(\partial_x h)^2 \end{cases}$$

Mass flux is directed from higher to lower μ

Surface diffusion

flux

typ. lifetime

size

$$V \propto -\mathrm{div}_S \boldsymbol{J} \propto \Delta_S \kappa^{(S)} \propto -\frac{\partial^4 h}{\partial x^4} \Rightarrow \tau = \mathrm{O}(\lambda^4)$$

velocity

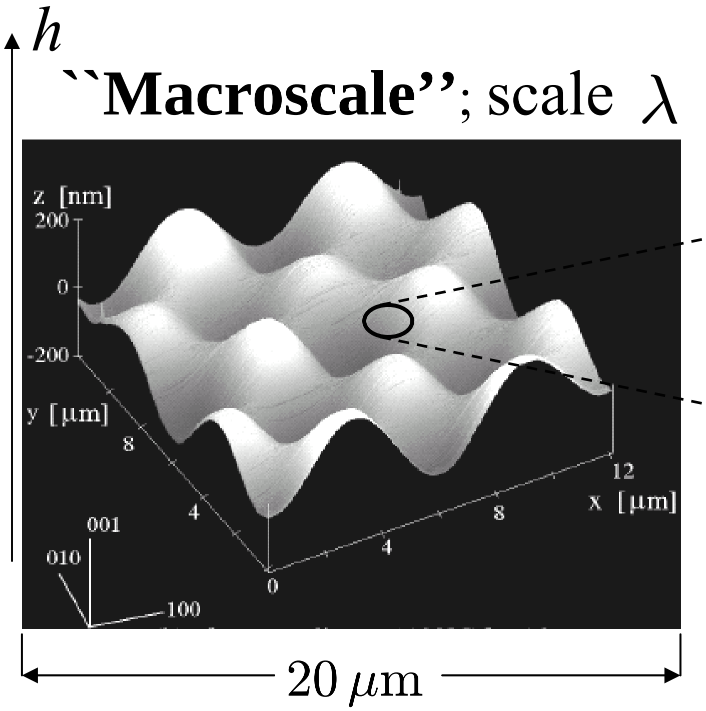
$$\boxed{\boldsymbol{J} = -\,\mathrm{const.}\,\nabla_S \mu}$$

$$\tau \propto \frac{\lambda^4}{D_s}$$

D_s surface diffusivity $\propto \exp\left(-\dfrac{\Delta E_{bar}}{k_{\mathrm{B}} T}\right)$

For **smaller** devices processing is `pushed' to **lower** temperatures, T.

$T < T_R$:Two scales and their relation

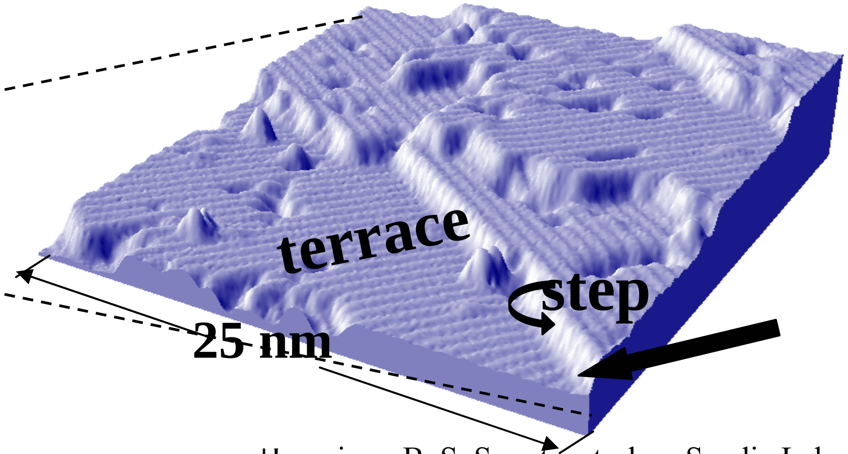


``Macroscale''; scale λ

20 μm

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

Nanoscale [same material/orientation]

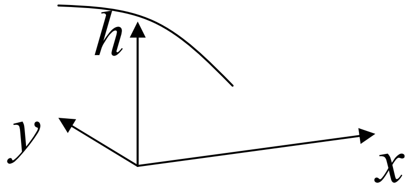


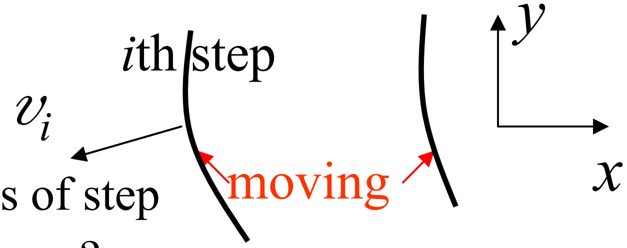
~1 atom;
height *a*

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

Steps modeled by
smooth curves [BCF, 1951]
Motion of ***steps***: ***Discrete scheme***

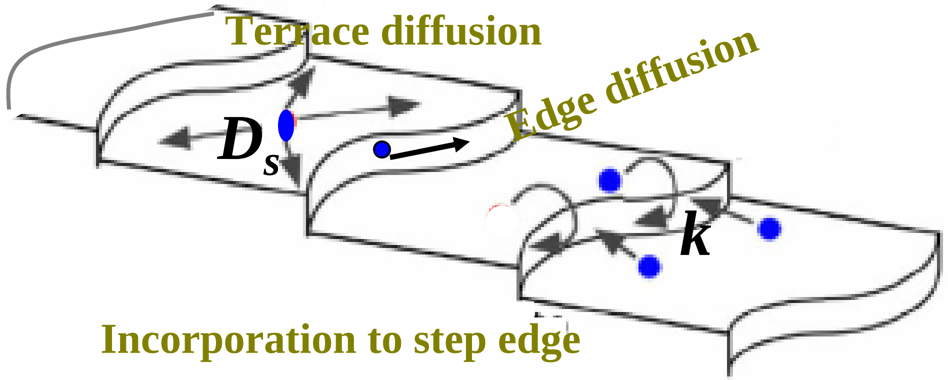
PDE for height *h*





: In terms of step
positions ?

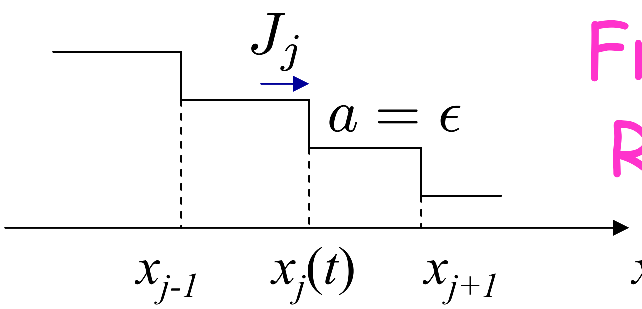
Microscopic processes [BCF, 1951]



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

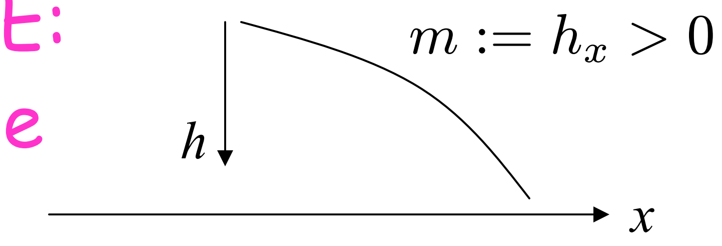
Steps move by mass conservation as atoms attach/detach

Combination of kinetic and energetic effects



$j=0,1,\dots,N$

From steps to PDE: Review of 1D case



Typical length λ

$\epsilon \to 0$

mass conservation

flux

$\dot{x}_j(t) \propto J_j - J_{j+1}\,,\; x = x_j \quad \Rightarrow \quad \partial_t h \propto -\partial_x J$

Attachment of atoms at steps

$J_j = k\cdot\left(\rho_j - \rho_j^{\text{eq}}\right),\;\; x = x_j \quad \Rightarrow \quad \boxed{J = -\frac{\rho_s}{\vartheta} M(|h_x|)\cdot\partial_x\mu}$

Fick's law

density

$\vartheta = k_B T$

Diffusion

$J_j = -D_s\cdot\partial_x\rho_j,\;\; D_s\partial_x^2\rho_j = \partial_t\rho_j \cong 0$

$M = D_s\left(1 + \frac{2D_s}{k\varepsilon}|h_x|\right)^{-1};\; \frac{D_s}{k\varepsilon} = O(1)$

chem. potential

$\rho_j^{\text{eq}} = \rho_s e^{\mu_j/\vartheta}, \quad |\mu_j| \ll \vartheta \quad (x_{j\text{-}1} < x < x_j)$

mobility

Energetics:
elastic dipole
nearest-neighb.
interactions

$\mu_j \propto \varepsilon^{-1}\left[\left(\frac{\varepsilon}{x_{j+1}-x_j}\right)^3 - \left(\frac{\varepsilon}{x_j - x_{j-1}}\right)^3\right] \Rightarrow \mu \propto -\partial_x\left(|h_x|h_x\right) \propto \left(\frac{\delta E}{\delta h}\right)_{L^2}$

$\sum_j \dot{x}_j\mu_j \propto \dot{E}_N;\;\; \mu_j \propto \delta E_N/\delta x_j$

[Nozières,1987; Rettori,Villain,1988; Ozdemir,Zangwil,1990; Spohn, 1991…]

ODEs for $x_j(t)$

4th-order PDE for $h(x,t)$

2 kinetic regimes: $D_s \ll (k\epsilon)m_j$ and $D_s \gg (k\epsilon)m_j$; $m_j := \epsilon/(x_j - x_{j-1})$

Diffusion limited (**DL**) Attachment-Detachment limited (**ADL**)

On coarse graining

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

$$X_j = \mathcal{X}(\underbrace{j\epsilon}_{h}) \ : \ X_{j+n} = \mathcal{X}(h) + (n\epsilon)\mathcal{X}'(h) + \frac{1}{2}(n\epsilon)^2\mathcal{X}''(h) + \ldots$$

Enforce $\epsilon \to 0$

- More careful treatment invokes weak formulation [DM,Kohn,2006]
- In **2D**, the large-scale surface mobility **M** is a **tensor** [DM,Kohn,2006].

No 1D analog (Lecture II)

- This approach is questionable if:

(i) parameters vary across terraces e.g., in case of surface reconstructions (Lecture II)

(ii) observation point lies **near facets** (Lecture III)

Continuum surface energy & relaxation

For *relaxation* in **DL** regime ($D_s/ka \to 0$), the PDE is of form:

$$\left.\begin{aligned} h_t &\propto \Delta\left(\frac{\delta E}{\delta h}\right)_{L^2} \\ E[h] &= \int g_1|\nabla h| + \frac{1}{3}|\nabla h|^3 \, d\mathbf{x} \end{aligned}\right\}$$

outside facets;
consistent with discrete step flow

This structure admits **extensions; surprises in 2D** (Lecture II)

Including facets:

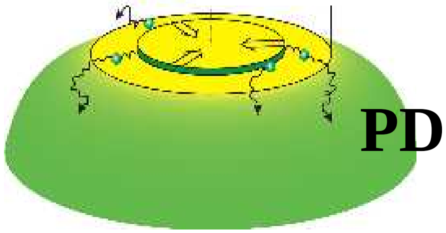
Fully continuum framework:

$$h_t \in -\partial_{H^{-1}} E \quad : \quad \text{subgradient of } E$$

[Kashima, 2005; Odisharia, 2006; 2nd-order: Kobayashi, Giga 1999; Giga, Giga, Kobayashi, 1999]

Subgradient formulation is not consistent
with step flow:
microstructure on top of facets (Lecture III)

[Israeli,Kandel,1999; DM,Fok,Aziz,Stone,2006]



Epilogue

- Step motion is described by **BCF** model [1951] and its extensions: near-equilibrium thermodynamics and kinetics for steps & terraces
- PDEs for surfaces must be **appropriate limits** of step flow. **Dimensionality** affects PDE structure crucially (**Lec. II**)
- Issues of continuum near facets (**Lec. III**) and with step instabilities
- Coarse graining is revised for surface-reconstruction inspired model: effective parameters are appropriate *averages* (more in **Lec. II**)
- Other approach: Renormalization group [Haselwandter, Vvedensky, 2006-7]
- Deviations from near-equilibrium kinetics can occur in actual materials. Extensions to far-from-equilibrium evolution must account for motion of kinks coupled with edge-atoms; extension of BCF

  [Caflisch, E, Gyure, Merriman, Ratch, 1999; Filimonov, Hervieu, 2004; Balykov, Voigt, 2005-6; Caflisch, Li, 2003; Kallunki, Krug, 2003; DM, Caflisch, 2008]