Modeling stepped surfaces across the scales

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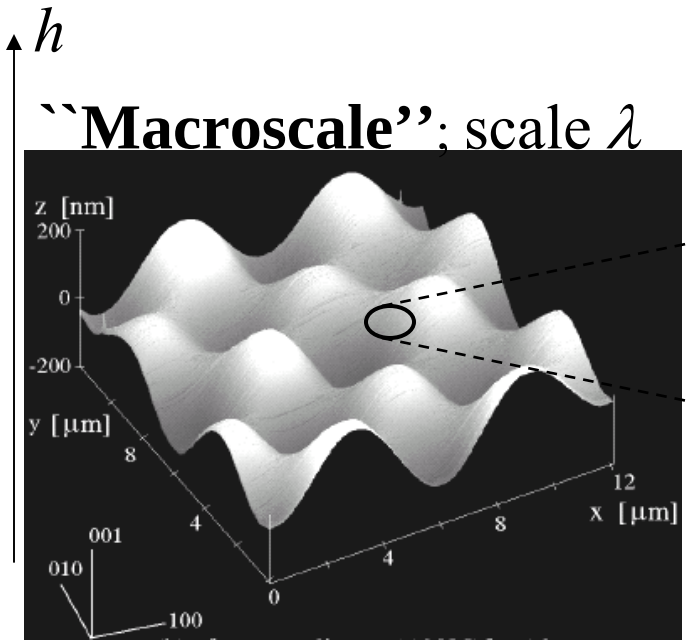
Steps on surfaces

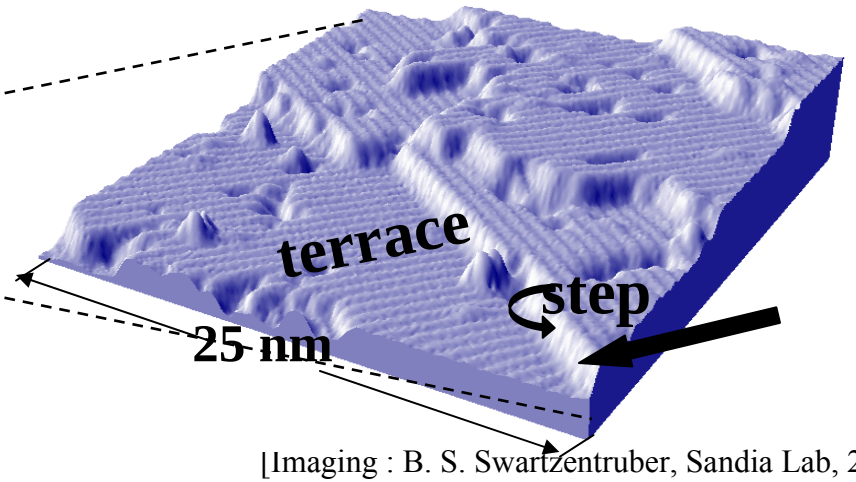


``Macroscale''; scale λ

20 μm

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

Nanoscale [same material/orientation]

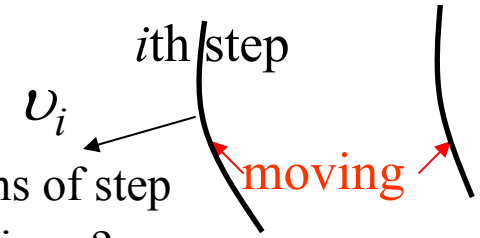


~1 atom;
height a

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

Continuum eqn. for height h ?

Motion of ***individual steps:***
discrete scheme



: In terms of step positions ?

A. For what continuum theory is step motion a consistent discrete solution scheme?

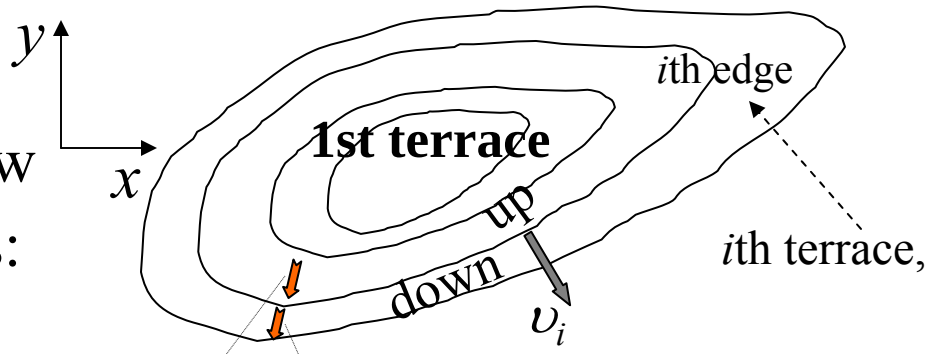
B. What are the effective material parameters ?

C. Where and how does the continuum break down ?

Step model (**BCF**-type theory)

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

Top view of steps:



- Step normal (scalar) **velocity** :

$$\upsilon_i \propto (J_{i-1})_\perp - (J_i)_\perp$$

(Neglect: Diffusion along edge)

- Adatom **flux** on *i*th terrace

$$\boldsymbol{J}_i(\boldsymbol{r},t) = -D_T \nabla \rho_i, \qquad D_T \Delta \rho_i = \frac{\partial \rho_i}{\partial t} \approx 0$$

Isotropic diffusion

Continuum relaxation in 2+1 dims

[DM, Kohn, 2006; DM, submitted]

- Mass conservation (from step velocity law):

$$\frac{\partial h}{\partial t} \propto -\nabla \cdot \boldsymbol{J}$$

- **Current** (from attachment-detachment at step edges):

Anisotropy

$$\boldsymbol{J} = \begin{pmatrix} J_\perp \\ J_{//} \end{pmatrix} = -\frac{D_T \rho_*}{k_B T} \begin{pmatrix} \frac{1}{1+Q\,m} & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \partial_\perp \mu \\ \partial_{//} \mu \end{pmatrix}; \qquad Q = \frac{2D_T}{\nu\, a},\ m = |\nabla h|$$

- **Chemical potential**:

$$\mu(\boldsymbol{r},t) \propto \left(-g_1 \nabla \bullet \frac{\nabla h}{|\nabla h|} - g_3 \nabla \bullet \left[\partial_m (m\mathsf{V}) \frac{\nabla h}{|\nabla h|} \right] \right)$$

$\mathsf{V} = \mathsf{V}(m)$ $\qquad \tilde{\beta}/a$

→ **PDE for *h***

outside facets

Elastic-dipole interactions (incl. beyond nearest neighbors):

$V = m^2$, $\quad g_3 > 0$ (repulsive)

PDE for crystal surface relaxation

$$\frac{\partial h}{\partial t} = -B\nabla\cdot\left\{\boldsymbol{M}\cdot\nabla\left[\nabla\cdot\left(\frac{\nabla h}{|\nabla h|}\right)+\frac{g_3}{g_1}\nabla\cdot\left(|\nabla h|\nabla h\right)\right]\right\}; \qquad h = h(x,y,t)$$

Material prmt.

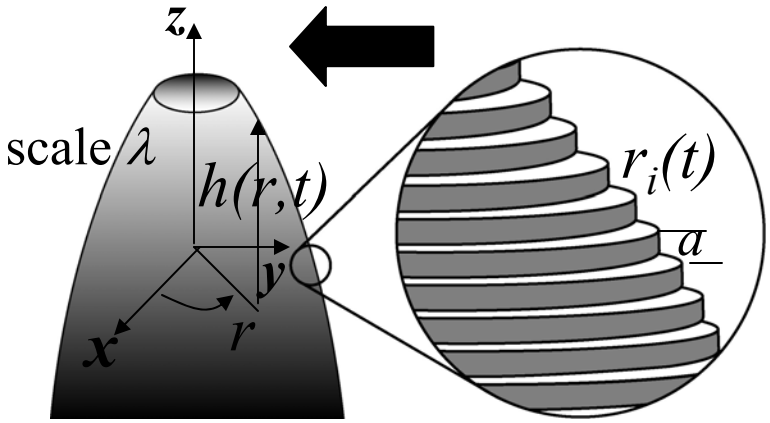
line tension

dipole step interactions

Cartesian coordinates :

$$\boldsymbol{M} = \frac{h_x^2}{|\nabla h|^2}\begin{pmatrix} \dfrac{1}{1+Q|\nabla h|}+\dfrac{h_y^2}{h_x^2} & -\dfrac{Q|\nabla h|}{1+Q|\nabla h|}\dfrac{h_y}{h_x} \\ -\dfrac{Q|\nabla h|}{1+Q|\nabla h|}\dfrac{h_y}{h_x} & \dfrac{h_y^2/h_x^2}{1+Q|\nabla h|}+1 \end{pmatrix}, \qquad Q=\frac{2D_s}{va},\ h_x \equiv \partial_x h$$

Facet evolution



Slow terrace diffusion:

$$D_T/(\nu a) << 1$$

PDE:

$m = |\partial h/\partial r|$:

$$\frac{1}{B}\frac{\partial h}{\partial t} = \frac{1}{r^3} + g\frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial}{\partial r}\frac{1}{r}\frac{\partial}{\partial r}(rm^2)$$

$$g = g_3 / g_1$$

Steepest descent: $\frac{\partial h}{\partial t} \propto \Delta \frac{\delta E}{\delta h}$

What are the right boundary conditions?

Discrete scheme:

$$\frac{dr_i}{dt} = -\frac{c}{r_i}(\Xi_{i+1} - \Xi_i);\ i = 3, 4, \ldots$$

$$\Xi_i = \frac{\mu_{i-1} - \mu_i}{\ln(r_i / r_{i-1})},$$

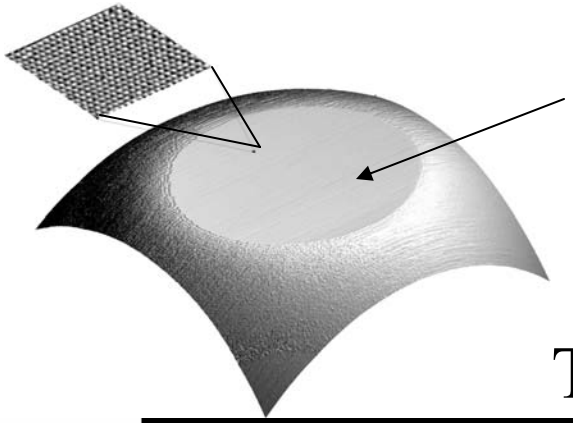
$$\mu_i = \frac{a^2 g_1}{r_i} + \frac{a}{2\pi r_i} g_3 \frac{\partial}{\partial r_i}[V(r_i, r_{i+1}) + V(r_i, r_{i-1})]$$

$$V(r_i, r_{i+1}) = \frac{r_i r_{i+1}}{(r_{i+1} - r_i)^2}$$

Crystal surfaces have facets: Microstructure effect

Imaging data from E. Williams, U. of Maryland NSF-MRSEC

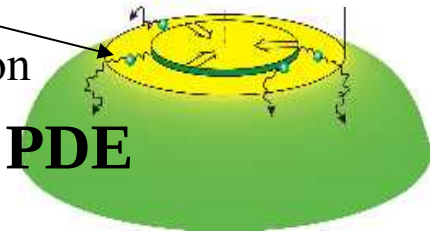
[Thurmer *et al.*, 2001]



facet

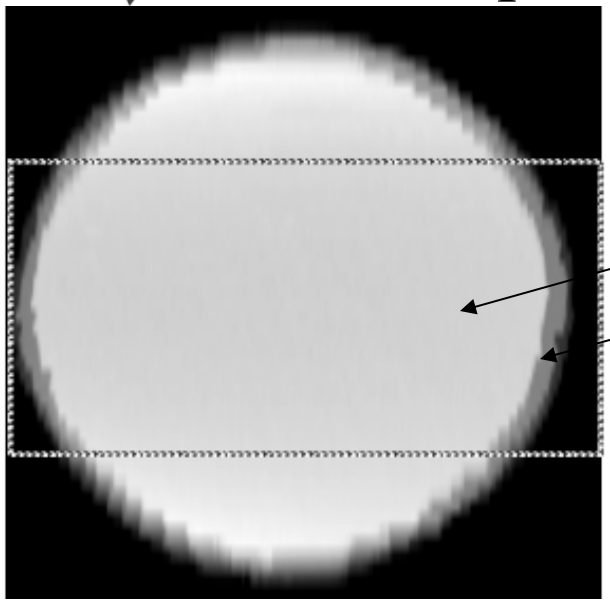
BC's:

Microscale motion



PDE

Top view



400 nm

Layers of atomic height:

Top layer

Next layer (grey)

Physically:

BC's at facet edge

must retain microscale details.

Choices of boundary conditions

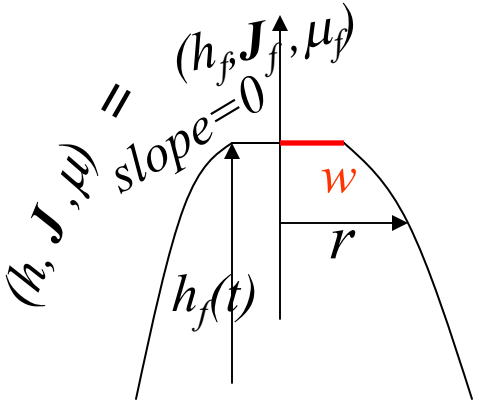
``Natural'' BC's (from steepest-descent formalism)

- Height continuity, $h(w,t)=h_f(t)$
- **Slope continuity**
- Current continuity, $\boldsymbol{J}=\boldsymbol{J}_f$

μ : `step chemical potential' outside facet

$$\boldsymbol{J} = -\frac{\rho_* D_T}{k_B T} \nabla \mu$$

- μ is extended **continuously** on facet



[Spohn, 1993; Kashima, 2004; Margetis, Aziz, Stone., 2004]

``Facet drop'' (fdr) condition:

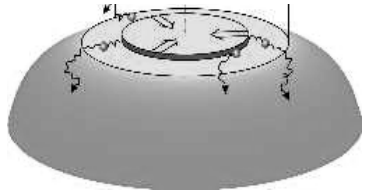
- Same

$$h_f(t_n)-h_f(t_{n+1})=a$$

time of nth step collapse

step height

replace



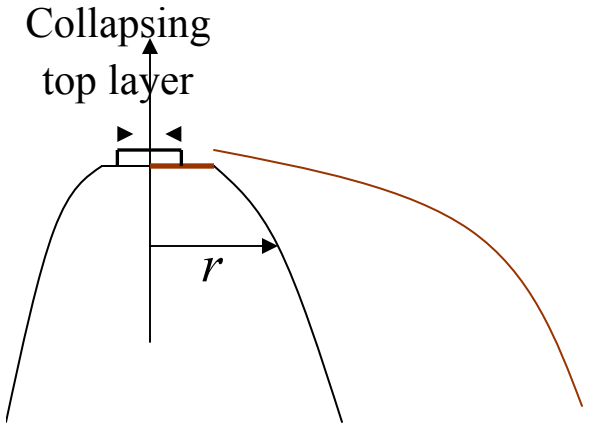
Need to know times t_n

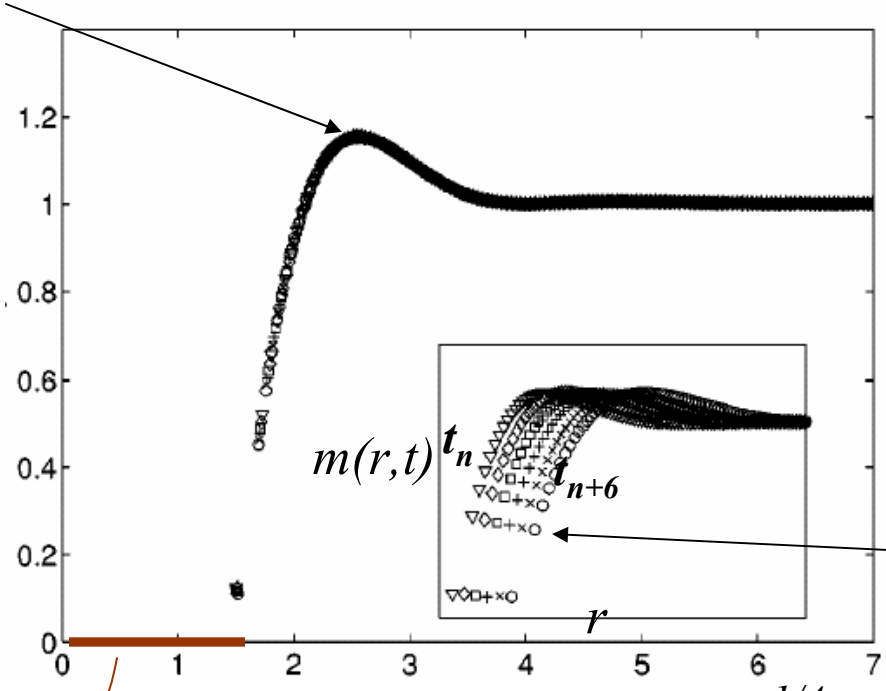
[Israeli, Kandel, 1999; Margetis, Fok, Aziz, Stone, 2006]

Self-similar solutions for long t

Data **collapse**;
initial cone

$m=\Lambda(\chi)$





facet

$\chi=r\ t^{-1/4}$

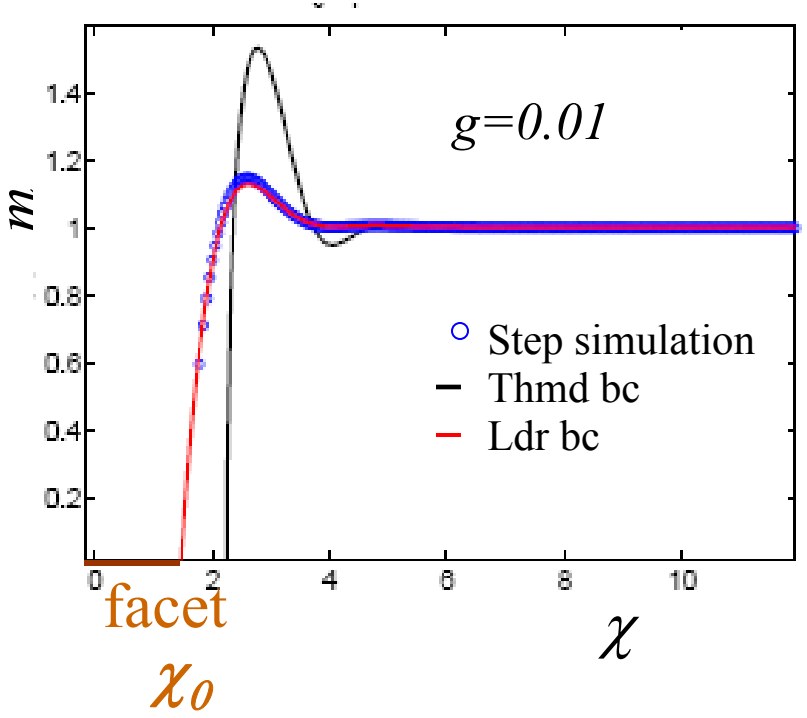
Data:
Numerical
simulations
of step motion

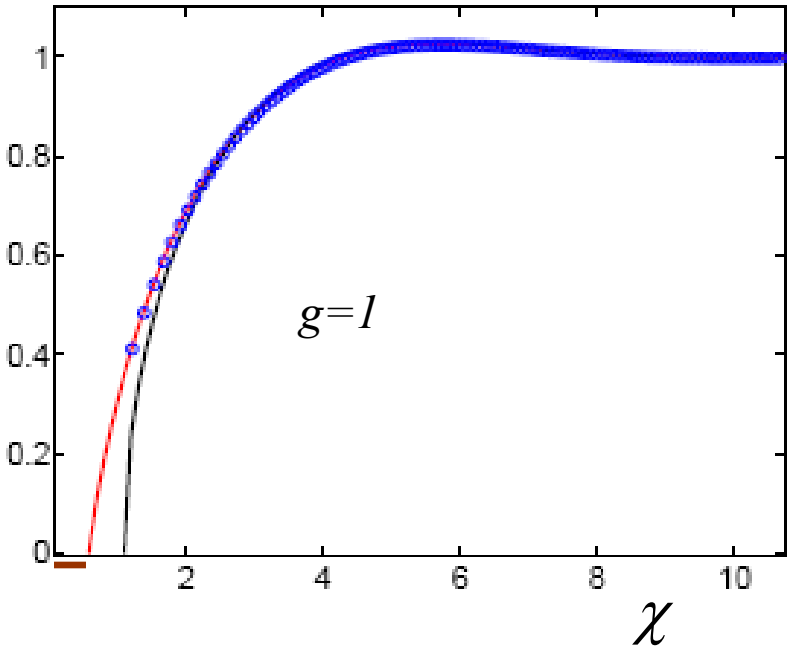
Collapse times: $t_n \sim t^* \cdot n^s, \quad n >> 1$

[Cone: Israeli, Kandel, 1999; Other shapes: Fok, Rosales, Margetis, *in preparation*]

Initial cone: $m = \Lambda(\chi = r\, t^{-1/4})$, $t_n \sim t^* n^4$ (PDE→ODE)

Continuum needs parameter t^* (from discrete eqs)

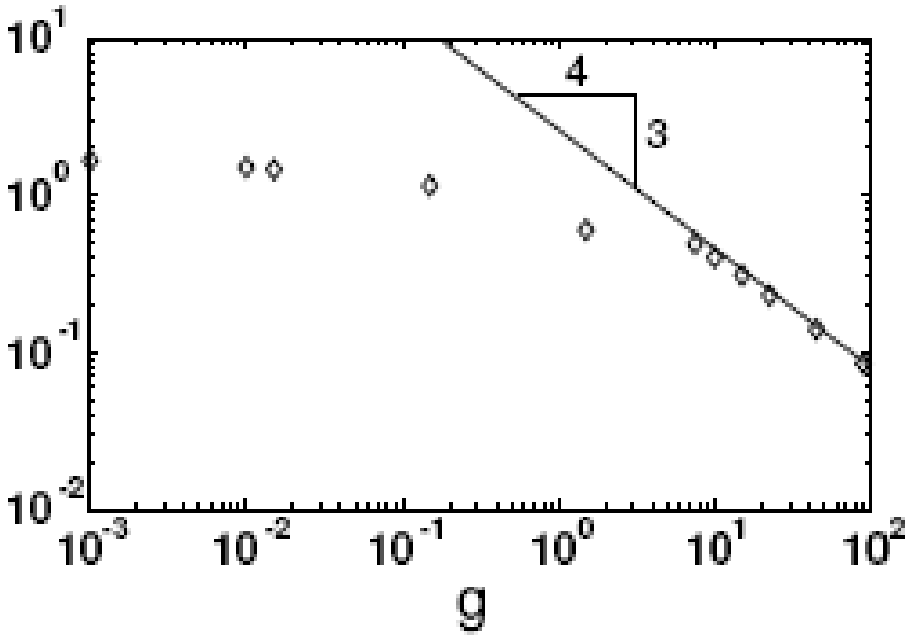




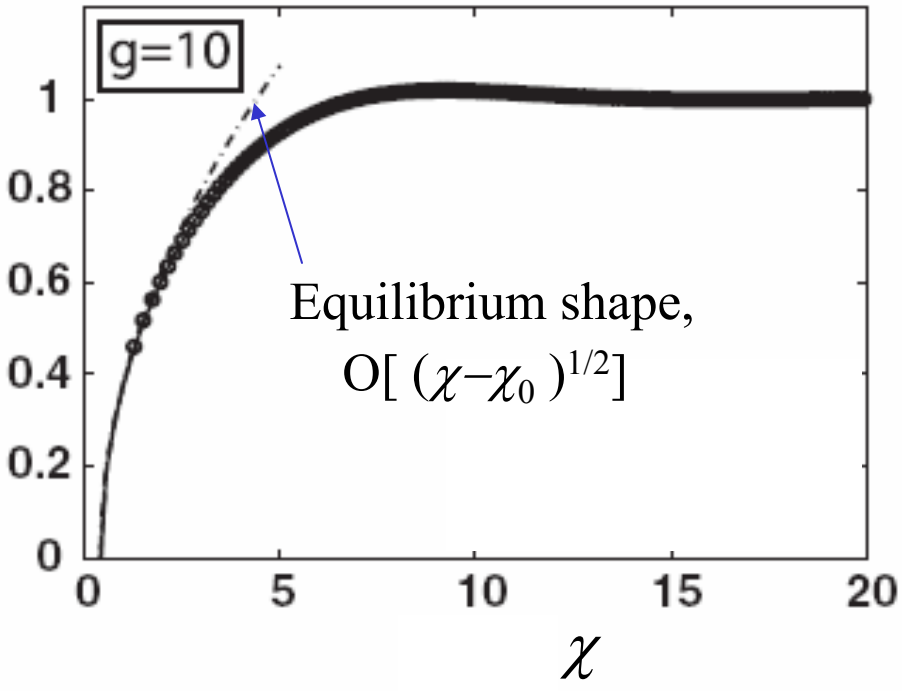
- Continuum needs NO adjustable parameter for $g >> 1$; facet **shrinks**.

[DM, Fok, Aziz, Stone, 2006]

Facet edge position χ_0



Slope m



A. For what continuum model is step motion a consistent discrete solution scheme?

B. What are effective material parameters ?

Effective parameters at nanoscale

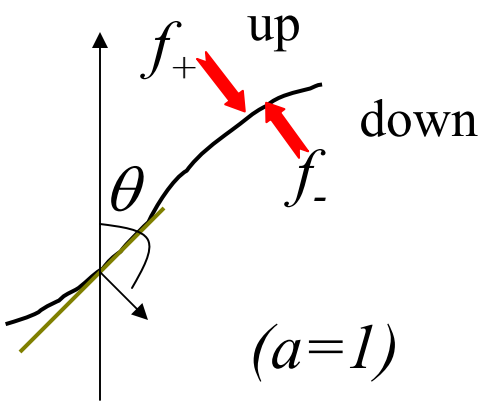
Motivation: crucial ingredient in modeling & simulations:

Adatom density

$$J_{\perp} = \pm f_{\pm} \propto \nu \cdot (\rho_{\pm} - \rho_{*} - \rho_{*} \frac{\tilde{\beta}}{k_B T} \kappa + \ldots)$$

Flux normal to step edge

Step ``stiffness''



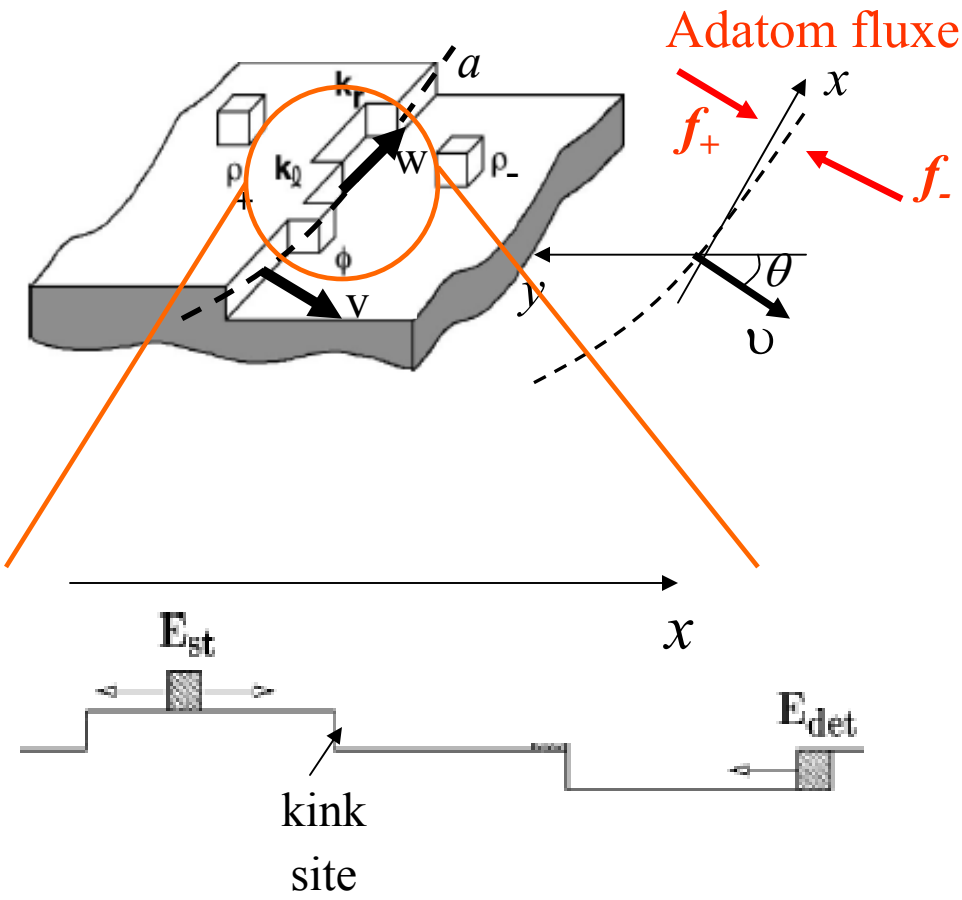
Effective equation for flux

Goal: derive $\tilde{\beta}(\theta)$ from a microscopic, kinetic model.

Model has to account for kinks and step edge atoms

Candidate model for far-from-equilibrium kinetics

[Caflisch et al., *PRE*, 1999; Balykov, Voigt, *Multisc. Model. Simul.*, 2006; Caflisch,Margetis *submitted*.]



+ Equations of motion for densities

+ Constitutive relations of fluxes with densities by **mean field** theory

Equations of motion for densities:

along edge

$$\begin{cases} \partial_t \phi - D_E \partial_x^2 \phi = f_\phi, \\ \partial_t k + \partial_x [w(k_r - k_l)] = 2(g - h), \end{cases}$$

f_ϕ : source flux of step edge atoms

D_E : step edge diffusion const. along x

$g,\ h$: gain and loss of kink pairs via nucleation/breakup etc

The model has:

- Kinetic steady state: Edges move at constant speed
- Equilibrium state (w/ detailed balance): Fluxes vanish

Constitutive relations (examples):

(Fluxes and velocity in terms of densities)

- f_ϕ : Source flux of step edge atoms

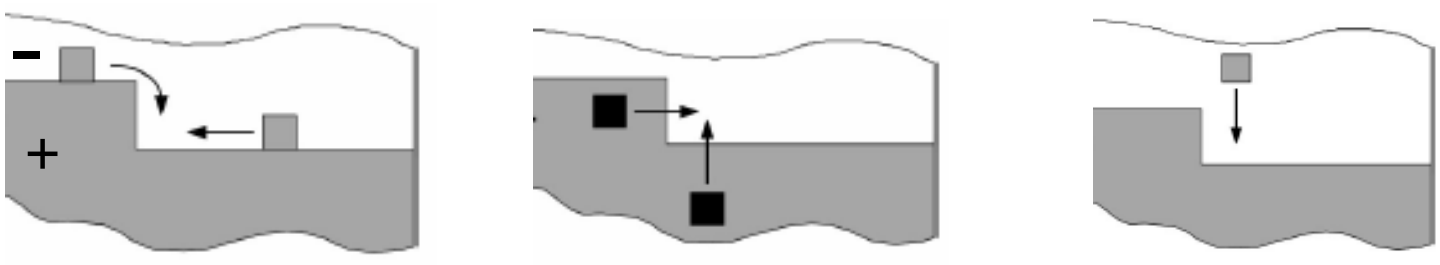
$$f_\phi = \underbrace{\frac{f_+ + f_-}{\cos\theta}}_{\text{Net flux of terrace adatoms to step edge atoms: +: upper terrace -: lower terrace}} - \underbrace{f_0}_{\text{Net flux of step edge atoms to kinks}}$$

- w : Kink velocity (along step edge)

[Caflisch *et al.*, 1999]

By **mean-field theory**: $w = w_1 + w_2 + w_3$

(Top view of step edge)



Edge atoms to **fixed** kink site

Upper-terrace adatoms to kink

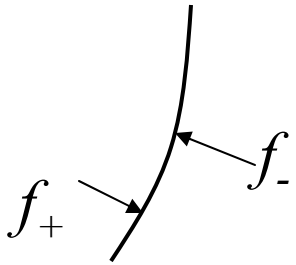
Lower-terrace adatoms to kink

$$w_1 \sim l_1 D_E \phi \qquad w_2 \sim l_2 D_T \rho_+ \qquad w_3 \sim l_3 D_T \rho_-$$

l_1, l_2, l_3 : coordination numbers (# of relevant sites)

Constitutive relations (continued):

- $f_{\pm}$: Flux of adatoms normal to an edge from upper (+) or lower (-) terrace



Above:
Top view of a step edge.

By mean-field theory:

$$f_{\pm} \sim (D_T \rho_{\pm} - D_E \phi)\cos\theta + \ldots$$

- υ : Step edge normal velocity (by mass conservation)

$$\upsilon = f_0 (1 + \phi\kappa\cos\theta)^{-1}\cos\theta$$

κ : Step curvature

FINALLY:

Constitutive relations ⟹ Sources in equations of motion & fluxes f_+ and f_- in terms of densities

Analytical derivation of stiffness $\tilde{\beta}$:

Perturbations around kinetic steady state

- Expand densities of kinks and step edge adatoms for small curvature:

$$k \approx k_0 + k_1\kappa, \qquad \phi \approx \phi_0 + \phi_1\kappa; \qquad \kappa : \text{suff. small}$$

Find coefficients by using **eqs of motion** and **constitutive relations**.

Assume: $P = \dfrac{Fw}{D_E} << 1$ (small ``Peclet number'') w: mean terrace width

- Enforce the **Gibbs-Thomson** formula :

$$f_\pm \sim \nu_\pm \cdot (\rho_\pm - \rho^{eq}), \qquad \rho^{eq} = \rho_* \exp\frac{\mu}{k_B T} \sim \rho_* \left(1 + \frac{\tilde{\beta}\,\kappa}{k_B T}\right)$$

Find $\tilde{\beta}=\tilde{\beta}(\theta)$ by comparison with formulas from kinetic model:

$$f_\pm \sim (D_T \rho_\pm - D_E \phi)\cos\theta + \ldots \sim [D_T \rho_\pm - D_E(\phi_0 + \phi_1\kappa)]\cos\theta + \ldots$$

Analytical results

$$\frac{\tilde{\beta}}{k_B T} \sim \begin{cases} (1/D_T \rho_*)\theta^{-1} & \theta_c = O(P^{1/3}) << \theta << 1 \\ (1/D_T \rho_*)c_0 & 0 \le \theta << \theta_c \end{cases}$$

if $(f_+ + f_-)_\theta|_{\theta=0} = O(1)$

Kinetic rates for attachment-detachment (ES effect):

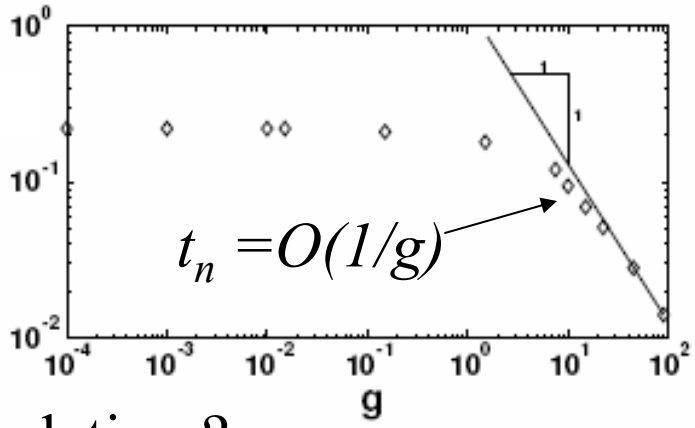
$$\nu_+ \sim D_T (1 + l_2 \tan\theta) \cos\theta \qquad \nu_- \sim D_T (1 + l_3 \tan\theta) \cos\theta$$

Take-Home Messages

- Continuum is **not self-contained**: Boundary conditions at facets need parameters (step collapse times, t_n) from discrete scheme

May t_n be evaluated independently?

Possibly, in limits $g<<1$ and $g>>1$.



Alternative (yet equivalent) BC's or formulation ?

Solutions beyond self-similarity?

- Step stiffness from perturbations of equilibrium state of kinetic model.

Other atomistic/kinetic models ?

Variational approach to relaxation

Surface free energy per unit projected area

$$G = g_0 + g_1 |\nabla h| + \frac{1}{3} g_3 |\nabla h|^3 \qquad E[h] = \iint dxdy \; G$$

convex

$$\mu = \mu_0 + \Omega \frac{\delta E}{\delta h}$$

$$\boldsymbol{J} \propto -\boldsymbol{M} \cdot \nabla \mu$$

tensor

From microscopic eqs.

$$\frac{\partial h}{\partial t} = -\nabla \cdot \boldsymbol{J}$$

PDE for h

$$\boldsymbol{M} = 1: \quad \frac{\partial h}{\partial t} \propto \Delta \frac{\delta E}{\delta h}$$

H^{-1} gradient flow

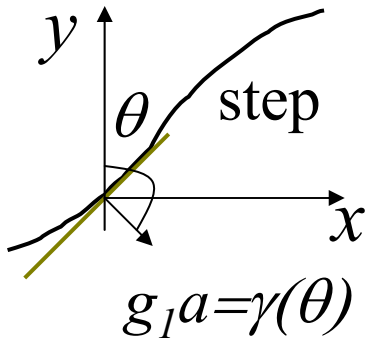
Extensions

- Line tension dependence on angle with crystallographic axis

Continuum:

$$\mu(\boldsymbol{r},t) \propto \left[-(\gamma + \gamma_{\theta\theta})\nabla \bullet \frac{\nabla h}{|\nabla h|} - g_3 \nabla \bullet \left(\partial_m (m V_0) \frac{\nabla h}{|\nabla h|} \right) \right]$$

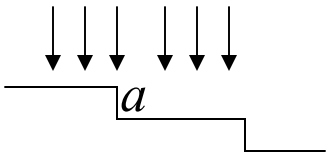
``stiffness'', $\tilde{\gamma}$



[DM, Kohn,2006]

- Ehrlich-Schwoebel effect: different rates for up- and down-step attachment-detachment: $k = 2(1/k_+ + 1/k_-)^{-1}$

- Deposition of material from above.



$$\boldsymbol{J} = \frac{Fa}{2} \frac{Q_+ - Q_-}{1 + Q|\nabla h|} \frac{\nabla h}{|\nabla h|}; \quad Q_{+(-)} = \frac{2D_s}{k_{+(-)} a}$$

[DM, Kohn, *in preparation*]

Strong step interactions ($g >> 1$) with self-similarity

ODE: $$-\frac{\chi}{4}\frac{dm}{d\chi} = \cancel{\frac{3}{\chi^4}} - g\frac{d}{d\chi}\frac{1}{\chi}\frac{d}{d\chi}\chi\frac{d}{d\chi}\frac{1}{\chi}\frac{d}{d\chi}(\chi m^2); \qquad \chi = r\,t^{-1/4}$$

line tension

step interactions

Dominant balance

$g >> 1$

On sloping surface

$$\xi := g^{-1/4}\,\chi$$

$$m(\chi;g) =: \tilde{m}(\xi) = O(1)$$

Both sets of BC's at facet edge reduce to:

$$\left.\begin{aligned} \tilde{m} &= 0 \\ (\tilde{m}^2)_\xi &= \frac{1}{g^{3/4}\chi_0} \end{aligned}\right\}$$

step inter. | line tension

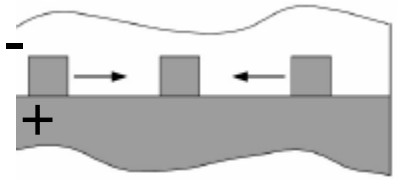
$\xi = \xi_0 = g^{-1/4}\chi_0$: facet edge

→ $\boxed{\chi_0 = O(g^{-3/4})}$

Constitutive relations (continued):

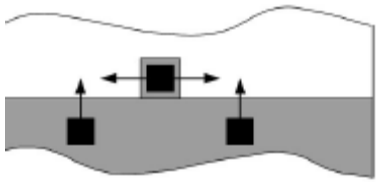
- g : Gain rate of kink pairs [Caflisch *et al. Phys. Rev. E*, 1999].

Distinct contributions to g by mean-field theory: $g=g_1+g_2+g_3$



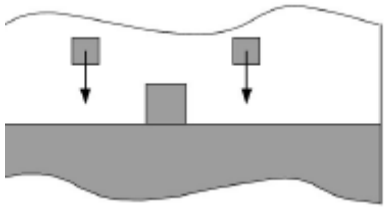
Edge adatoms hop to fixed edge adatom

$$g_1 = m_1 D_E \phi^2$$



Upper-terrace adatoms hop to fixed edge adatom

$$g_2 = m_2 D_T \rho_+ \phi$$

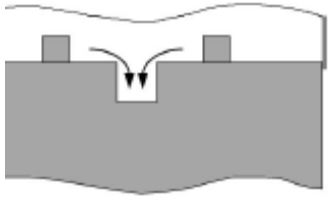


Lower-terrace adatoms hop to fixed edge adatom

$$g_3 = m_2 D_T \rho_- \phi$$

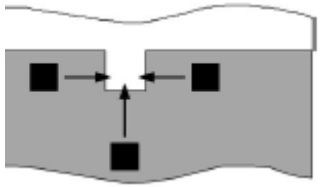
- h: Loss rate of kink pairs

By mean-field theory: $h=h_1+h_2+h_3$



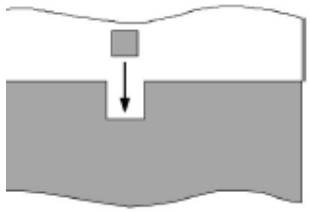
Edge adatoms hop to empty site between kinks

$$h_1 = n_1 D_E \phi k_r k_l$$



Upper-terrace adatoms hop to empty site

$$h_2 = n_2 D_T \rho_+ k_r k_l$$



Lower-terrace adatoms hop to empty site

$$h_3 = n_3 D_T \rho_- k_r k_l$$