The trouble with crystal facets

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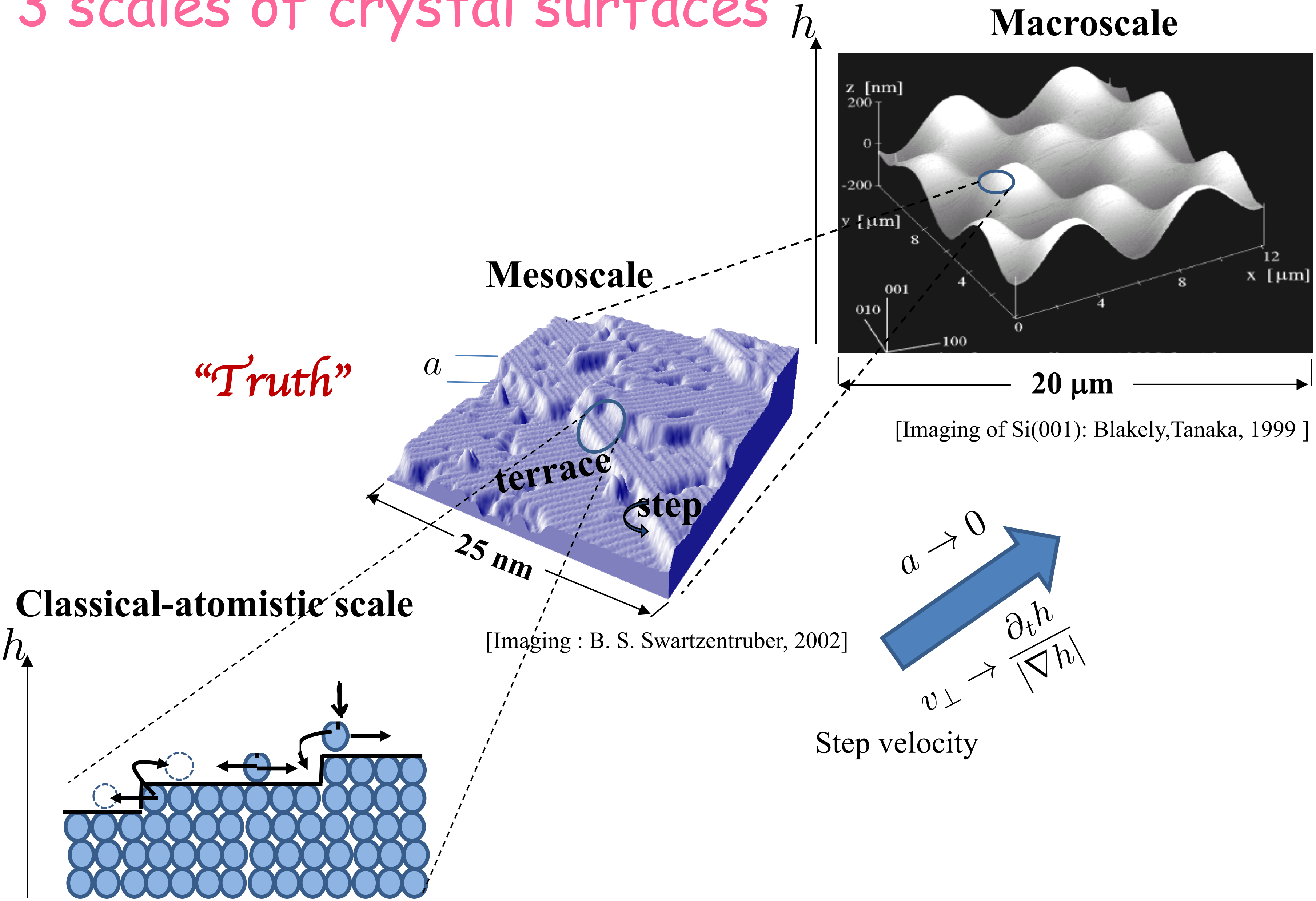
3 scales of crystal surfaces



Macroscale

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

Mesoscale

“Truth”

[Imaging : B. S. Swartzentruber, 2002]

Classical-atomistic scale

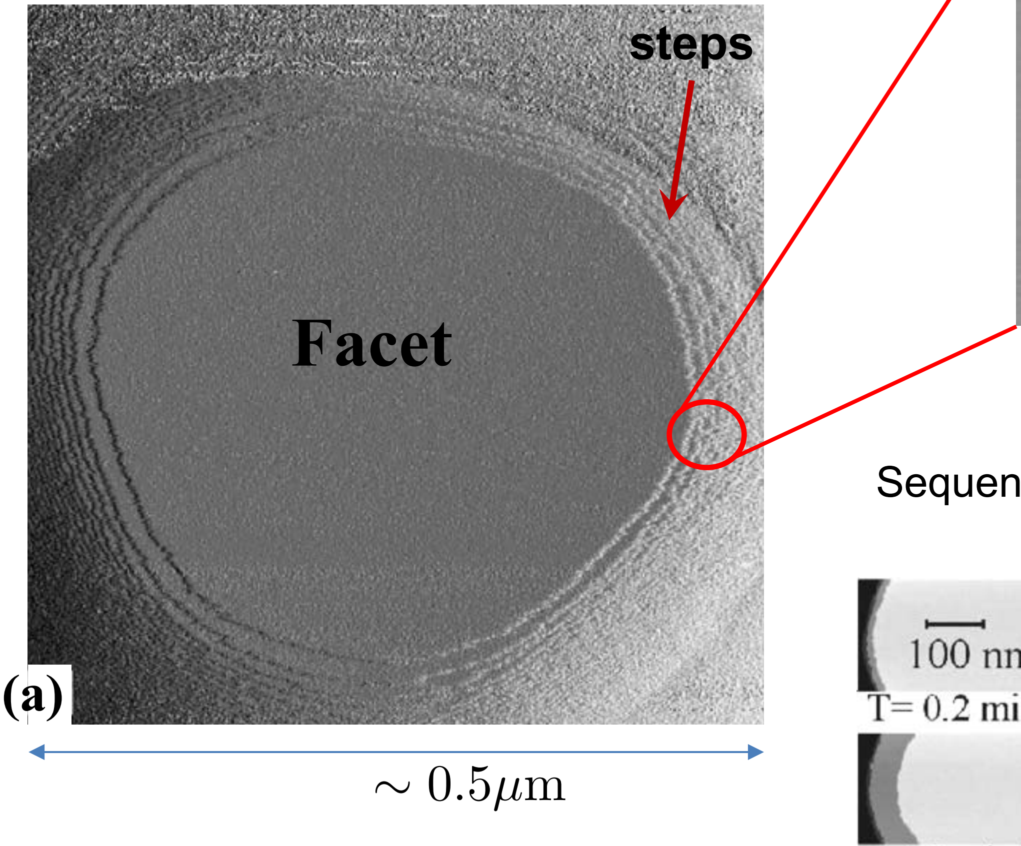
$a \to 0$

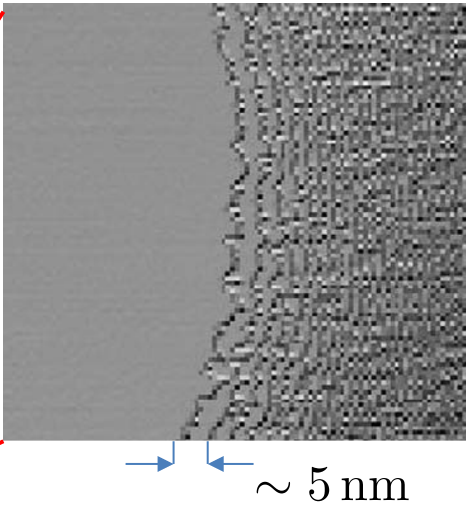
$v_\perp \to \frac{\partial_t h}{|\nabla h|}$

Step velocity

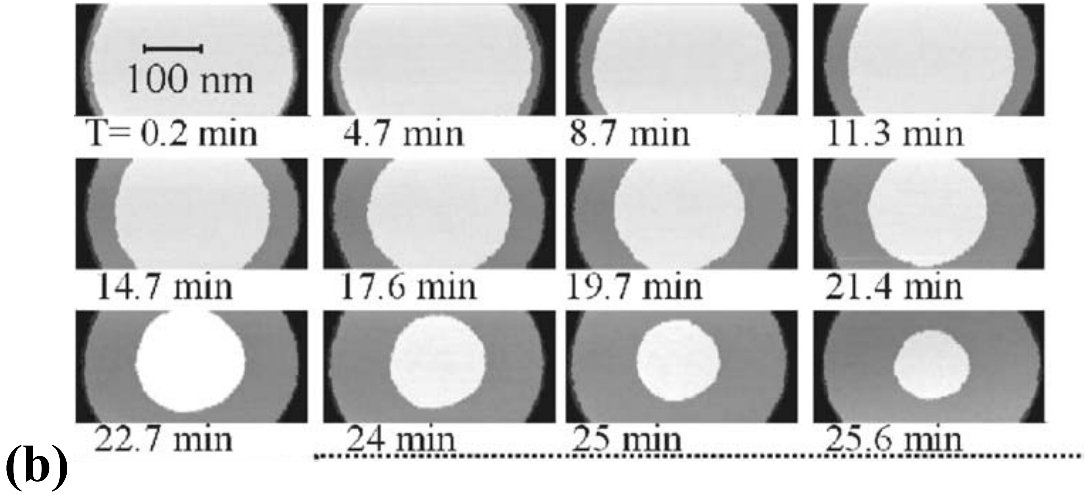
Crystal facets (macro-plateaus)

STM image: faceted Pb crystallite (top view) [Bonzel, 2003]



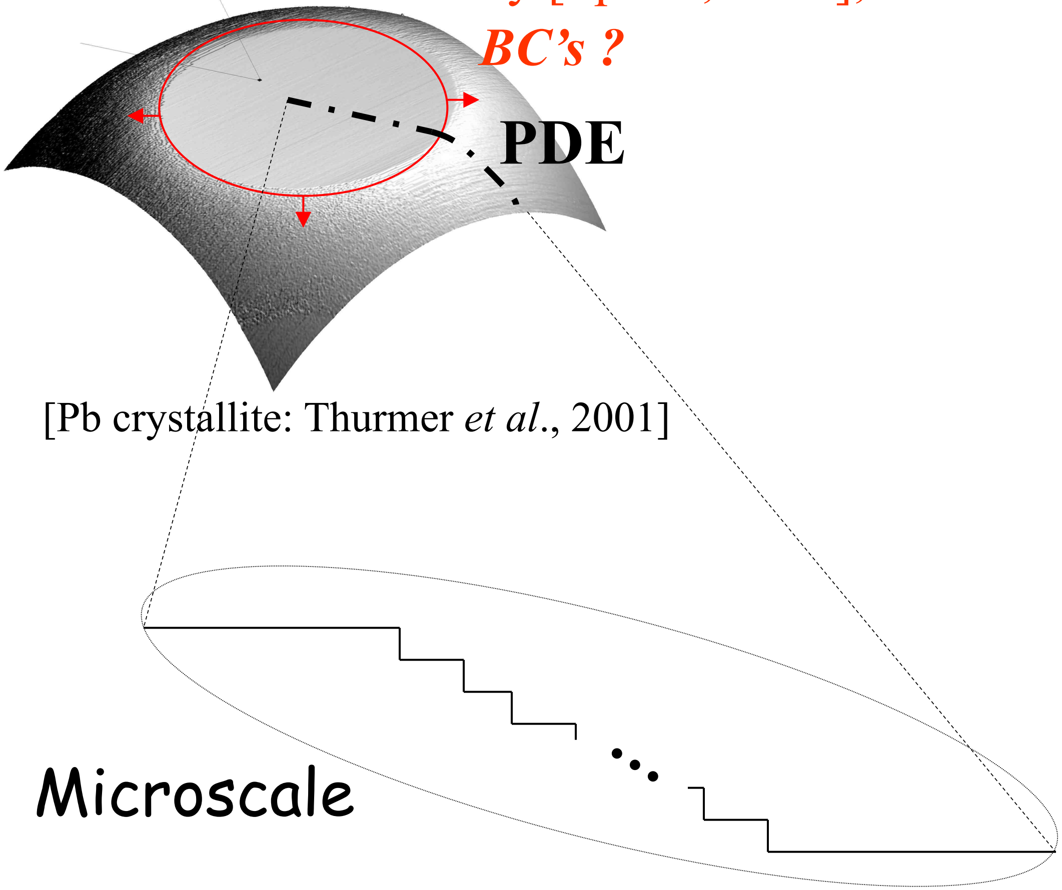


Sequence of STM images: Single-layer peeling on facet [Thurmer *et al*. 2001]



Crystal facets: Modeling

Macroscopic view:



free boundary [Spohn, 1993];

BC's ?

PDE

[Pb crystallite: Thurmer *et al*., 2001]

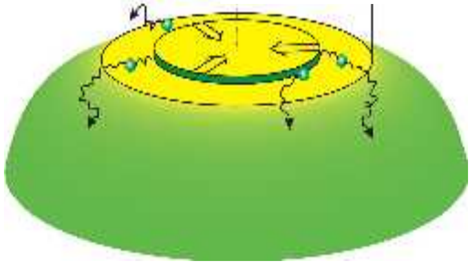
Microscale

[Fok,Rosales,DM, 2008; Al Hajj Shehadeh, Kohn, Weare, 2011]

[Selke, Duxbury, 1995; Chame, Rousset, Bonzel, Villain, 1996/97; Chame, Villain, 2001]

Complication:

Microscale motion on top



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

Scope

- Continuum laws for crystal surface morphological evolution are often viewed as limits of step motion.

- Facets are special parts of the crystal surface.

What predictions for facet evolution arise from PDE models?
How is facet evolution linked to step motion?
Heuristics…

Take-home message (roughly)

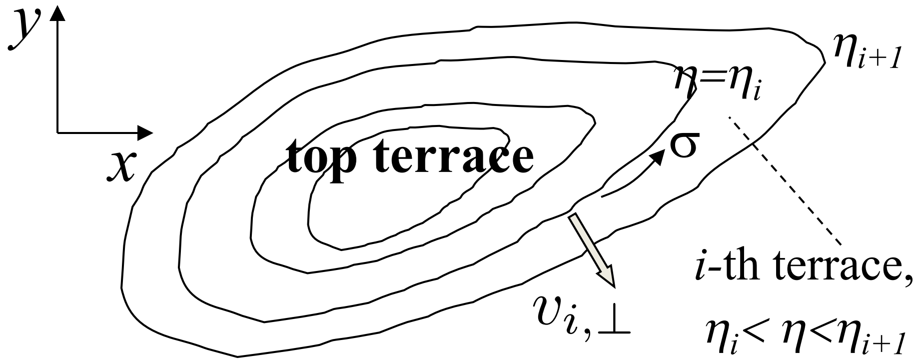
It has not been possible to develop a general theory so far;

our understanding has relied on specific settings…

Step flow: BCF model

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

Local coordinates (η, σ);
descending steps of height a;
i-th step at $\eta = \eta_i$



- Step normal **velocity** :

$$v_{i,\perp} = a^2(J_{i-1,\perp} - J_{i,\perp})$$

- Adatom **diffusion**

  on i-th terrace: $\mathbf{J}_i = -D_s \nabla \rho_i, \; D_s \Delta \rho_i + F = \frac{\partial \rho_i}{\partial t} \approx 0 \quad \eta_i < \eta < \eta_{i+1}$

- Robin-type boundary conditions at bounding step edges :

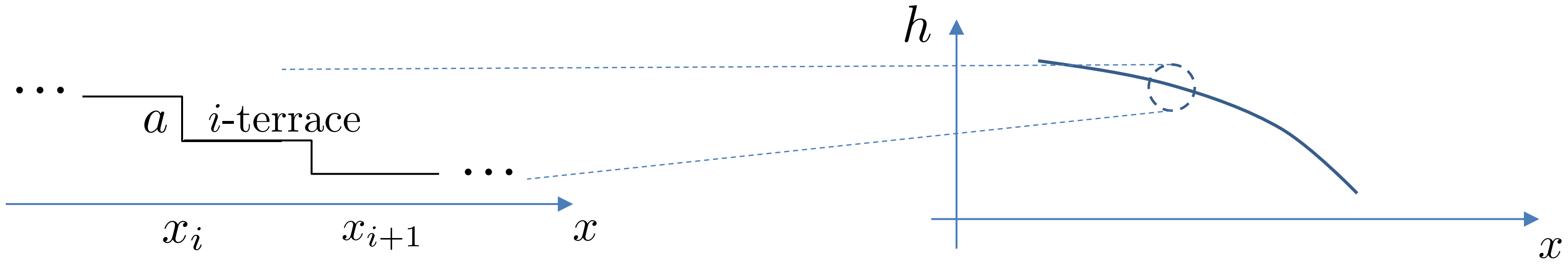
$$-J_{i,\perp}^{+} = q_{+}[\rho_i^{+} - \rho_i^{\text{eq}}(\sigma,t)], \; \eta = \eta_i; \; J_{i,\perp}^{-} = q_{-}[\rho_i^{-} - \rho_{i+1}^{\text{eq}}(\sigma,t)], \; \eta = \eta_{i+1}$$

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

Gibbs-Thomson relation

$\mu_i(\sigma,t)$: step chemical potential: change of i-th step energy per atom

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



Step velocity

Mass flux on i-th terrace

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

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

$$\xrightarrow{a \to 0}$$

$$\frac{a}{x_{i+1} - x_i} = \mathcal{O}(1)$$

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

Mass conservation

Attachment/detachment

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

$$\frac{D_s}{qa} = \mathcal{O}(1)$$

$$\Rightarrow \quad J = -\frac{D_s}{1 + \cancel{\frac{D_s}{qa}|\partial_x h|}} \partial_x \rho^{\mathrm{eq}}$$

Diffusion-limited kinetics

"Fick's law" for surface diffusion

Step chemical potential, near equilibrium

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

step chem. potential

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

Total step energy (N steps)

Elastic dipole-dipole interaction: (nearest-neighbor)

$$E_N^{\mathrm{st}} = \sum_{i=0}^{N-1} \frac{g}{(x_{i+1} - x_i)^2} , \; g > 0$$

$$\Rightarrow$$

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

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

$$E[h] = \tilde{g} \int |\partial_x h|^3 \, dx$$

Relaxation PDE in 2+1 dims, away from facet

[DM, Kohn, 2006]

Total step energy

$a \to 0$

Ill-defined on facet

$$\boxed{\frac{dE_N^{\mathrm{st}}}{dt} = \sum_i \int_{step\, i} v_{i,\perp}\, \mu_i \,\mathrm{d}s} \Longrightarrow \boxed{\mu_i \to \mu = \left(\frac{\delta E}{\delta h}\right)_{L^2}}$$

step veloc.

Step chemical potential

$$E[h] = \int \gamma(\nabla h)\, \mathrm{d}x = \int \{g_1|\nabla h| + (g_3/3)|\nabla h|^3\}\, \mathrm{d}x$$

Facet: $\nabla h = 0$

$\mathbf{J}_i \propto -\nabla \rho_i$, $\mathrm{div}\mathbf{J}_i = 0$ on terrace;

$$J_{i,\perp} \propto \rho_i - \underbrace{\rho_s(1+\mu_i/T)}_{\approx\, \rho_i^{\mathrm{eq}}}$$ at step

(linearization)

$$\Longrightarrow \boxed{\mathbf{J} = -\mathbf{M}(\nabla h)\cdot \nabla \mu}$$

Tensor mobility

Flux (Fick-type law)

$$\boxed{v_i = J_{i-1,\perp} - J_{i,\perp}} \Longrightarrow \boxed{\frac{\partial h}{\partial t} = -\mathrm{div}\mathbf{J}}$$

mass conservation

4th-order, parabolic-like PDE for h

Gradient flow of $E[h]$

Alternatively (more generally):

$$J_{i,\perp} \propto \rho_i - \rho_{\mathrm{s}} e^{\mu_i/T} \Longrightarrow \mathbf{J} \propto -\mathbf{M}(\nabla h)\cdot \nabla e^{\mu/T}$$

Can facet evolution be described by a "fully" continuum theory?

Linearized Gibbs-Thomson relation:

- By PDE theory: Yes, via "extended gradient formalism" based on continuum-scale **singular surface energy**, $E[h]$.

[Kobayashi, Giga, 1999; Spohn, 1993; Shenoy, Freund, 2002; Odisharia, Thesis, 2006; DM, Aziz, Stone, 2005; Kashima, 2004; Giga, Giga, 2010; Giga, Kohn, 2011]

- By step flow: Not always. Microscale condition for motion of top steps may be needed

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

Extended-gradient formalism in typical settings

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

surface diffusion: DL kinetics

"Natural" boundary conditions at facet edges follow.

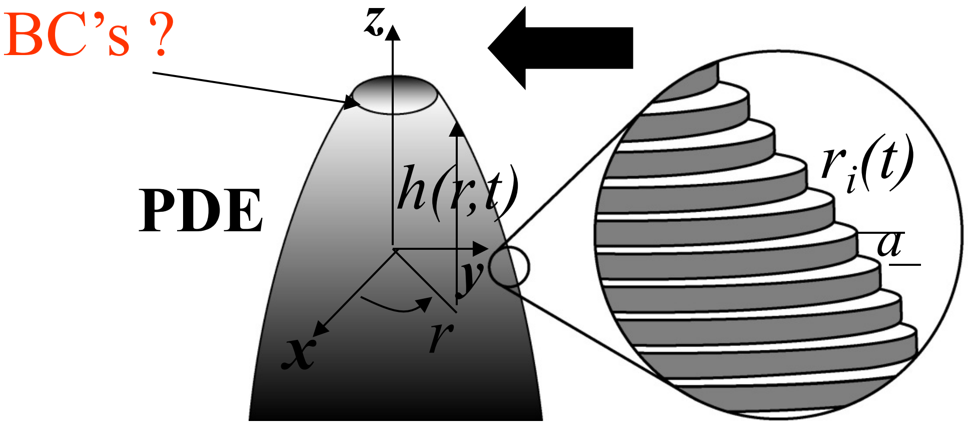
What should the above rule amount to, practically?

Suppose the facet is smoothed out by 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.

I. Facets and step flow

[Schneider, Nakamura, DM, 2014]

Surface diffusion: DL kinetics in radial geometry



Discrete scheme:

$$\boxed{\frac{\partial h}{\partial t} = -\Omega\,\mathrm{div}\,\mathbf{j},\ \ \mathbf{j} = j\mathbf{e}_r;} \qquad (\Omega = a^3)$$

$$j = -\frac{D_s\rho_s}{k_BT}\frac{\partial\mu}{\partial r};$$

$$\mu = \Omega\frac{\delta E}{\delta h} = \Omega g_1\,\mathrm{div}\boldsymbol{\xi},\ \boldsymbol{\xi} = \xi\,\mathbf{e}_r$$

PDE

$$\frac{\partial h}{\partial t} \propto \Delta\frac{\delta E}{\delta h} \quad \textcolor{red}{H^{-1}\ \text{gradient flow}}$$

$$E[h] = \int \left[|\nabla h| + (g/3)|\nabla h|^3\right]\mathrm{d}x\ ;\ g = \frac{g_3}{g_1}$$

$$\dot{E} = \left(\frac{\delta E}{\delta h}, h_t\right)_{L^2} = -\left\|\Delta\frac{\delta E}{\delta h}\right\|^2_{H^{-1}} \leq 0$$

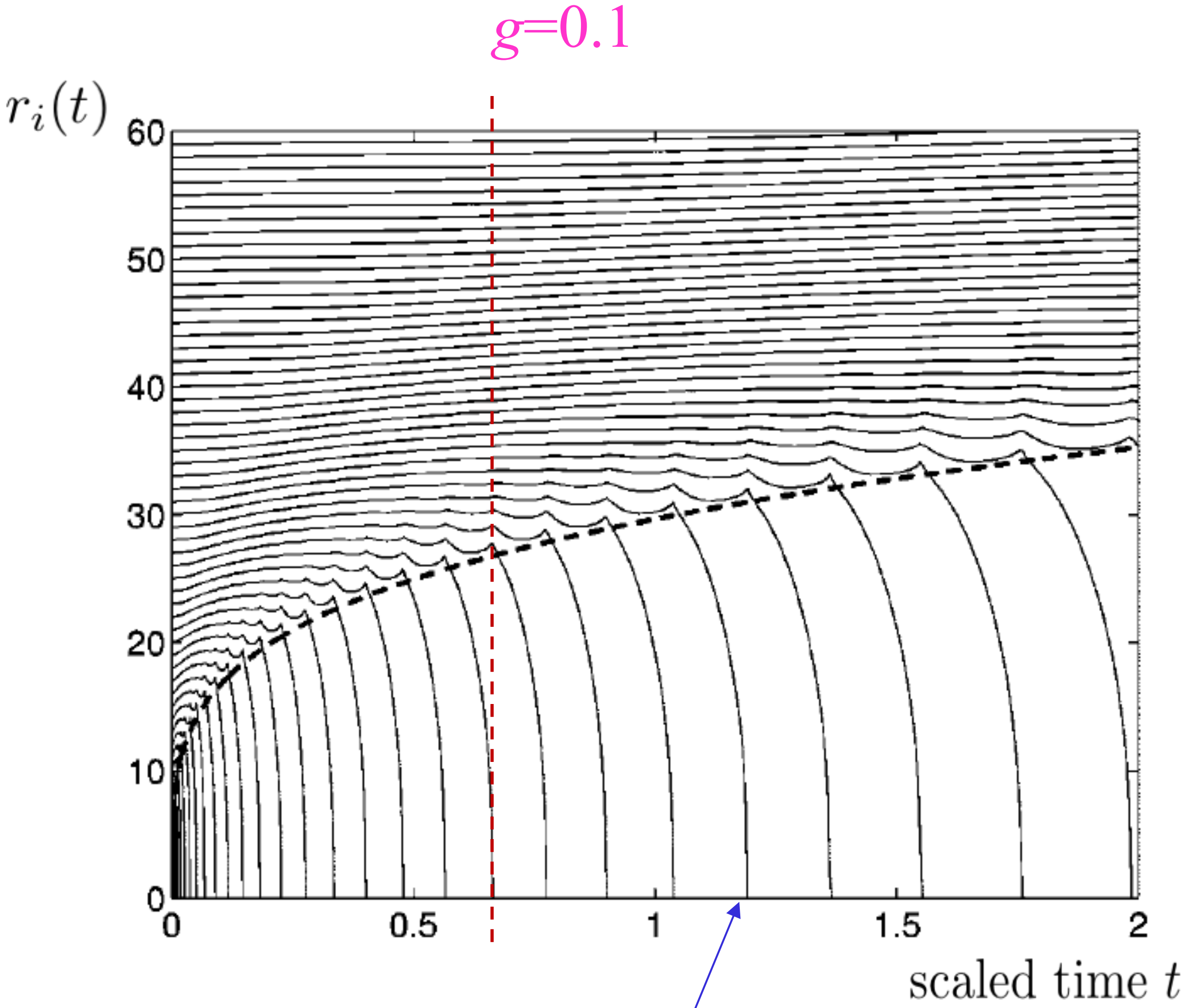
$$\boxed{\frac{\mathrm{d}r_i}{\mathrm{d}t} = -\frac{D_s\rho_s a^2}{k_BT}(J_{i+1} - J_i)}$$

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

Diffusion-limited kinetics; linearized model

$$\mu_i = \underbrace{\frac{a^3g_1}{r_i}}_{\text{Step curvature}} + \frac{a^3}{2\pi r_i}\underbrace{g_3\frac{\partial}{\partial r_i}[V(r_i,r_{i+1}) + V(r_i,r_{i-1})]}_{\text{Nearest-neighbor, elastic-dipole step-step interactions}}$$

Step trajectories

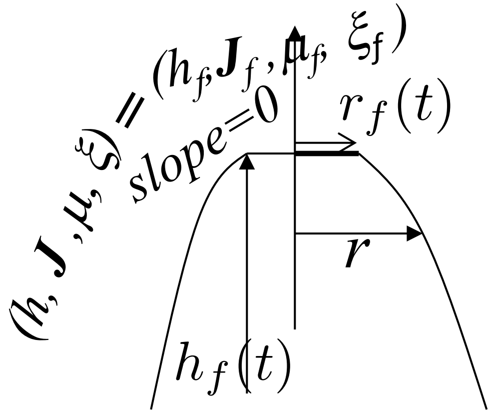


i-th step collapse time, t_i
(relative to initial configuration)

Free-boundary approach: Boundary conditions

Natural BC's in radial setting

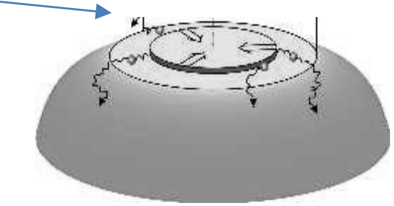
- Height continuity: $h(r_f^+, t) = h_f(t)$
- Slope continuity
- (Normal) Mass-flux $e_r \cdot \mathbf{J}$: cont.
- $\mu = -\mathrm{div}\boldsymbol{\xi}$: extended continuously onto facet
- $e_r \cdot \boldsymbol{\xi} = \xi$: continuous



[Spohn, 1993; Shenoy, Freund, 2002;
DM, Aziz, Stone., 2005; DM, Fok,Aziz,Stone, 2006]

Jump conditions for μ, ξ

Collapse times t_n



Keep

Introduce:

$$\mu(r_f(t)^-, t) = Q(t)^{-1}\, \mu(r_f(t)^+, t)$$

$$\xi(r_f(t)^-, t) = Q(t)\, \xi(r_f(t)^+, t)$$

$$Q(t) = \frac{1}{2}\left\{\frac{r_{n+2}(t_n) + r_{n+1}(t_n)}{2r_{n+2}(t_n)} + \frac{r_{n+1}(t_n) + \cancel{r_n(t_n)}}{2r_{n+1}(t_n)}\right\}$$

$t_n \le t < t_{n+1}$

time of
n-th step collapse

In close agreement with step simulations;

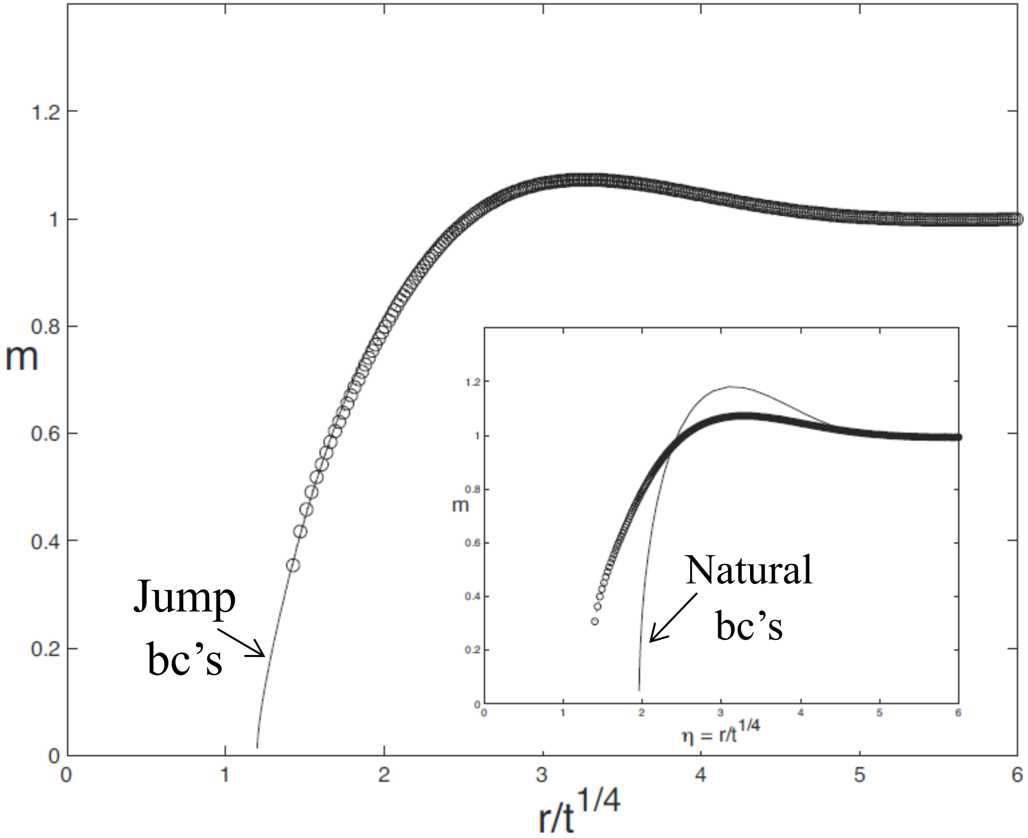
$Q(t) \approx$ const., $n \gg 1$

Numerics: conical initial data; self-similar regime (long *t*)

Discrete slopes behave as self-similar for long times

Ansatz: $m(r,t) \approx \mathfrak{M}(rt^{-1/4})$

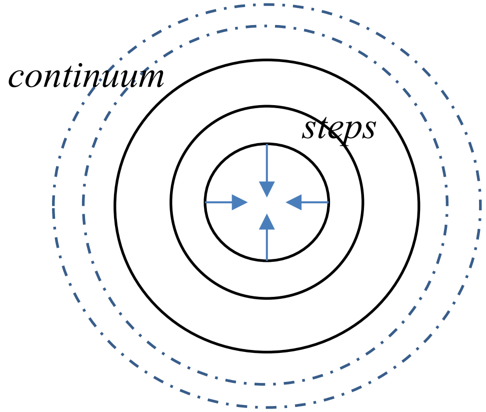
g=0.1



Can we reconcile these two scales via resolving only few top steps?

“Hybrid” iterative scheme

Top view



1. Compute self-similar slope $m(r,t)$ near facet via natural bc’s

2. Simulate M top steps, typically M = 3, terminated by

$$r_{n+M+l+1} = r_{n+M+l} + \frac{a}{m(r_{n+M+l}, t)} \; ; \; l = 0,\, 1 \; , \; \tilde{t}_{n_0} < t \leq \tilde{t}_{n_*} , \; n_0 \leq n < n_*$$

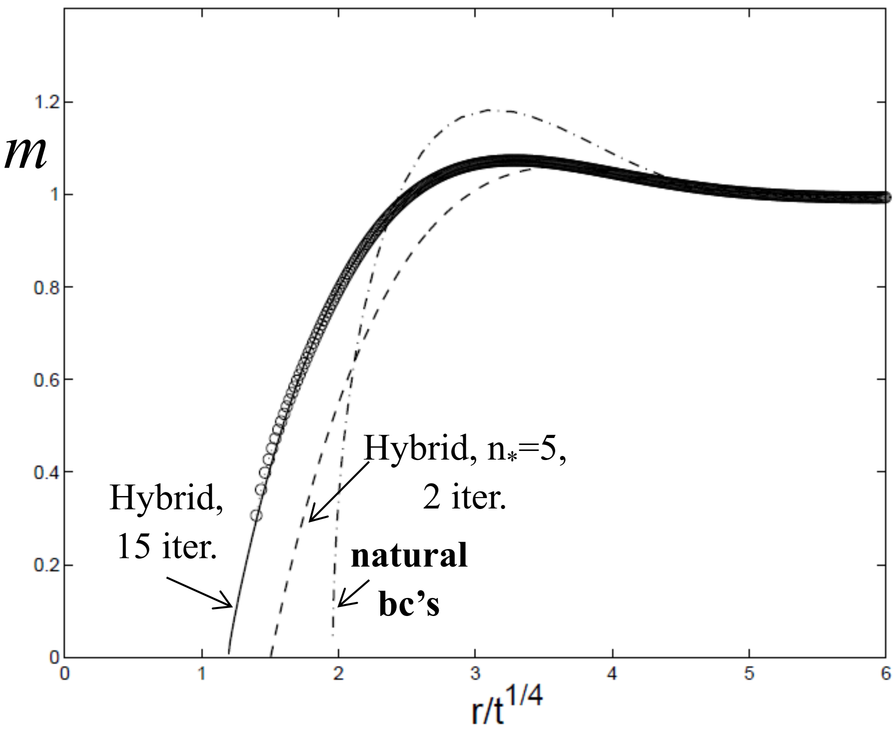
Initiation: $n_0 = 0 \; , \; n_* \geq 1 \; ; \; \tilde{t}_0 = 0$

3. Re-compute self-similar slope m using jump conditions at: $t = t_{n_*}$

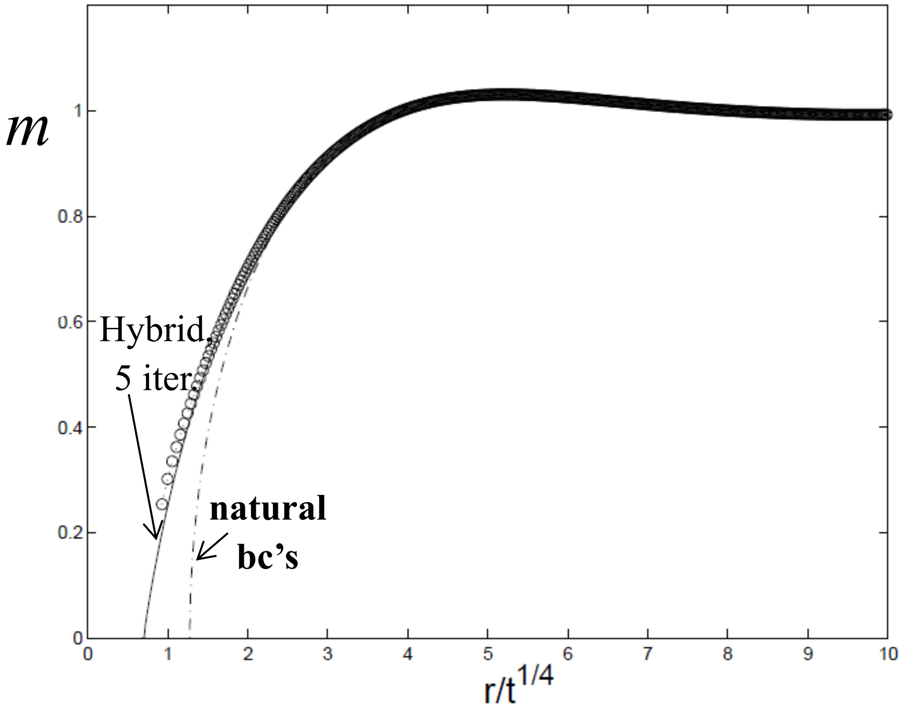
4. Repeat: stage 2 with n_0 replaced by previous n_* , and n_* by n_*+1;
and stage 3. Iterate, advancing t.

Numerics; conical initial data - long *t*

g=0.1



g=1



Conclusion and Pending issues. I.

- **PDE boundary conditions at facets may need step microstructure:** Microscale motion can be incorporated into jump discontinuities of thermodynamic quantities, via discrete geom. factor in DL regime.

- Thus far, progress has been made in **radial** setting, DL kinetics, **self-similar** regime. Boundary conditions have been speculated (empirically), motivating a **hybrid** iterative scheme (few steps).

- Would the jump conditions emerge from limits of step flow?

- Does the hybrid scheme really converge? Why?

- Extensions to earlier times; richer kinetics, fully 2D setting?

II. A PDE prediction (heuristics): Asymmetry in crystal facets in 1+1 dimensions

[Liu, Lu, Marzuola, DM, *preprint*]

“Exponential-PDE” model for surface diffusion; DL-regime

$$\partial_t h = \Delta \exp\left[\underbrace{-\beta \mathrm{div}\left(\boxed{\frac{\nabla h}{|\nabla h|}} + g|\nabla h|\nabla h\right)}_{\beta\frac{\delta E}{\delta h}}\right] \quad ; \quad \beta = T^{-1},\ g \geq 0$$

$$; \quad E[h] = \int \gamma(|\nabla h|)\,\mathrm{d}x \ , \ \gamma(p) = p + (g/3)p^3$$

What are the plausible predictions by this PDE?

$$\dot{E} = \left(\frac{\delta E}{\delta h}, h_t\right)_{L^2} = \left(\frac{\delta E}{\delta h}, \Delta e^{\beta(\delta E/\delta h)}\right)_{L^2} = -\beta \int \left|\nabla \frac{\delta E}{\delta h}\right|^2 e^{\beta(\delta E/\delta h)}\,\mathrm{d}x \leq 0$$

Set $\beta = 1$

Reduction to 1+1 dimensions; periodic profile

$$\partial_t h = \partial_{xx} \exp\left[-\partial_x\left(\frac{\partial_x h}{|\partial_x h|}\right)\right]$$

Neglect of $|h_x|h_x$ term

Assume $h(-x,t) = h(x,t)$

Goal:

Formulate a system of ODEs for facet height and position via free-boundary view

Formalism (across facet):

$$\partial_t h = -\partial_{xxx} v \ ; \quad \partial_x v = -e^{-\partial_x \xi} \ , \ \xi(h_x) \in \partial\gamma(h_x) \ ; \partial\gamma(p) = \begin{cases} \{\mathrm{sgn}(p)\}, & |p| > 0 \\ [\text{-}1, 1], & p = 0 \end{cases}$$

How may one pick element ξ?

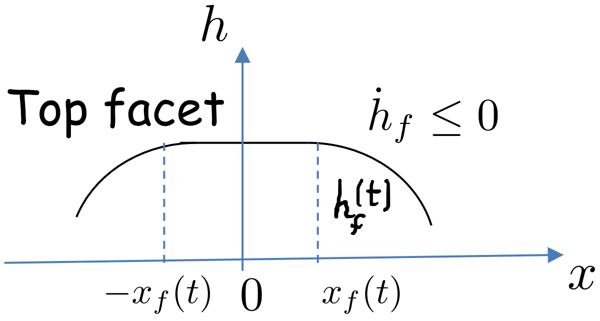
Claim: (By analogy with H^{-1} gradient flow) Find $\xi = \tilde{\xi}(x,t)$ s.t. $\partial_x v^* = -e^{-\partial_x \tilde{\xi}}$ where v^* is the minimizer of functional $\mathcal{F} : D \to \mathbb{R}$ defined by

$$\mathcal{F}[v] = \int_{-\ell}^{\ell} (\partial_{xx} v)^2 \, \mathrm{d}x \ , \quad D(F) = \{v \in H^2[-\ell, \ell] : \ v \text{ is odd and } \partial_x v(\pm\ell) = 1\}$$

Claim: "natural" BC's:

- Facet speed by mass conservation
- $\mu(x,t) = -\partial_x \tilde{\xi}(x,t)$ and $\tilde{\xi}(x,t)$: continuous in x

Free-boundary approach (construction of a solution)



Assumptions:

- Facet is symmetric in x, $h(-x,t) = h(x,t)$.
- Facet has zero slope, $\partial_x h = 0$.
- $\xi(p) = p/|p|$ (p: slope) is extended onto facet as odd function on $\mathbb{R}$; $\tilde{\xi}(x,t) = \xi(\partial_x h)$.

PDE structure: $\boxed{\partial_t h = -\partial_x J,\ J = -\partial_x e^{\mu},\ \mu = -\partial_x \tilde{\xi};}$ $h(x,0) = h_0(x)$

On **top facet**, $-x_f(t) \leq x \leq x_f(t)$:

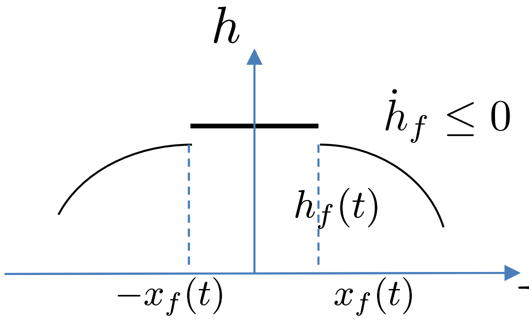
$$\left\{\begin{array}{l} \dot{h}_f = -\partial_x J \Rightarrow J(x,t) = -x\dot{h}_f + C_1(t);\ C_1(t) = 0 \text{ (by symmetry)} \\ \partial_x e^{\mu} = -J \Rightarrow \mu(x,t) = \ln\left[\dfrac{x^2}{2}\dot{h}_f + C_2(t)\right]; \\ \partial_x \tilde{\xi} = -\mu \Rightarrow \tilde{\xi}(x,t) = -\displaystyle\int_0^x \ln\left[\dfrac{s^2}{2}\dot{h}_f + C_2(t)\right] ds + C_3(t);\ C_3(t) = 0 \end{array}\right.$$

Apply:

Mass conservation: $\dot{x}_f[h_0(x_f) - h_f] = \dot{h}_f x_f$

Continuity of $\tilde{\xi}(\cdot,t)$ and $\mu(\cdot,t) \Rightarrow C_2(t) = 1 - x_f^2\dot{h}_f/2$

Free-boundary approach: ODEs



ODE system for (x_f, h_f), **top** facet $(\dot h_f \le 0)$:

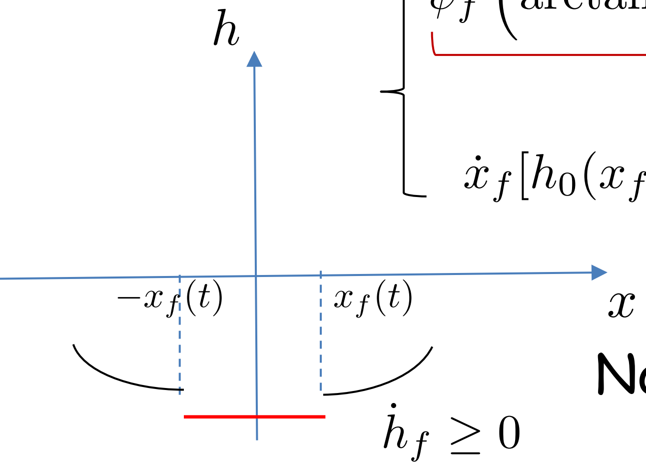
$$\begin{cases} 2\sqrt{1+X_f^2}\,\ln\left(\sqrt{1+X_f^2}+X_f\right)-2X_f=\sqrt{\dfrac{|\dot h_f|}{2}}\ ; \quad X_f:=x_f\sqrt{\dfrac{|\dot h_f|}{2}} \\ \dot x_f[h_0(x_f)-h_f]=\dot h_f\,x_f \end{cases}$$

The top facet **expands**

The bottom facet behaves **differently:**

ODE system for (x_f, h_f), **bottom** facet $(\dot h_f \ge 0)$:

$$\begin{cases} \underbrace{\psi_f\left(\arctan\psi_f-\dfrac{\pi}{2}\right)+1}_{Q(\psi_f)\ ;\quad \text{monotone},\ 0<Q(\psi_f)\le 1}=\dfrac{1}{2x_f}\ ; \quad \psi_f:=\dfrac{\sqrt{1-X_f^2}}{X_f}\ ,\ X_f:=x_f\sqrt{\dfrac{\dot h_f}{2}} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (\text{if } X_f\neq 0) \\ \dot x_f[h_0(x_f)-h_f]=\dot h_f\,x_f \end{cases}$$



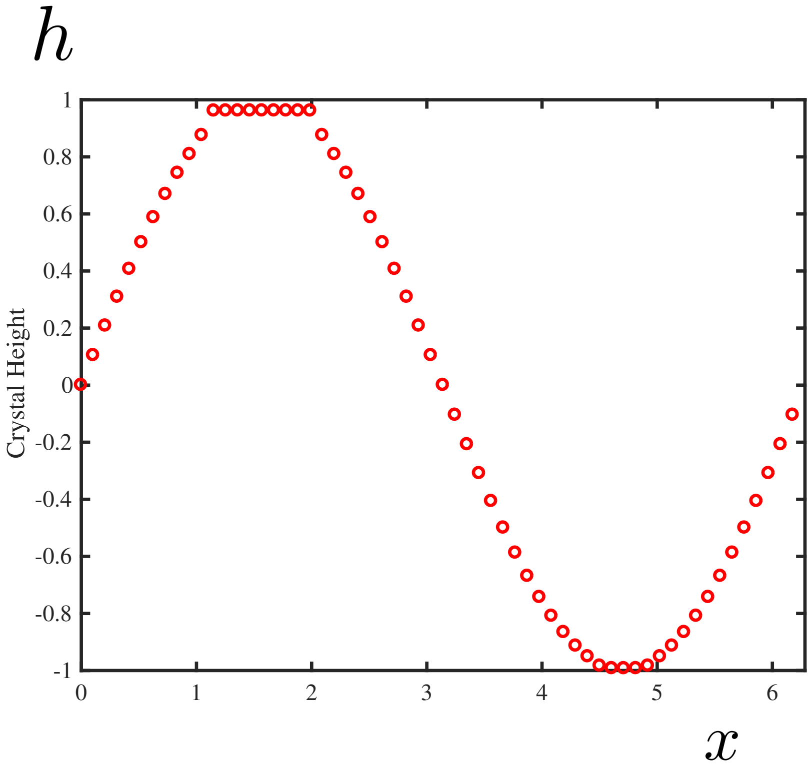
No evolution if facet size is below a "critical" value

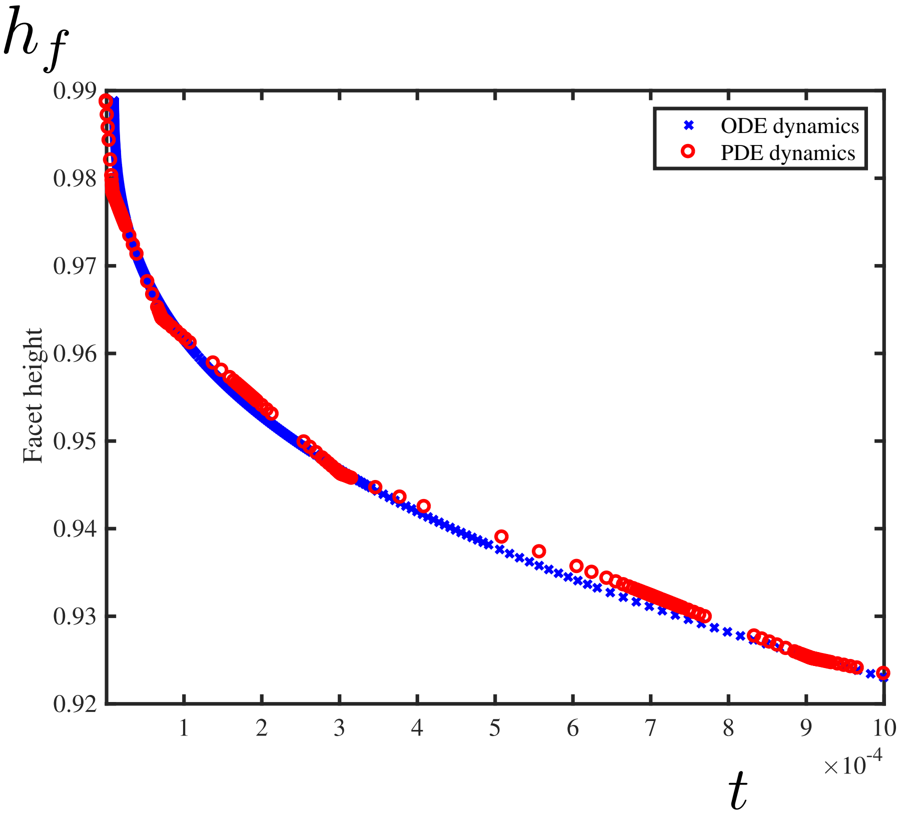
Numerical simulations of PDE vs ODEs

Numerics for PDE: Via regularization of $E[h]$

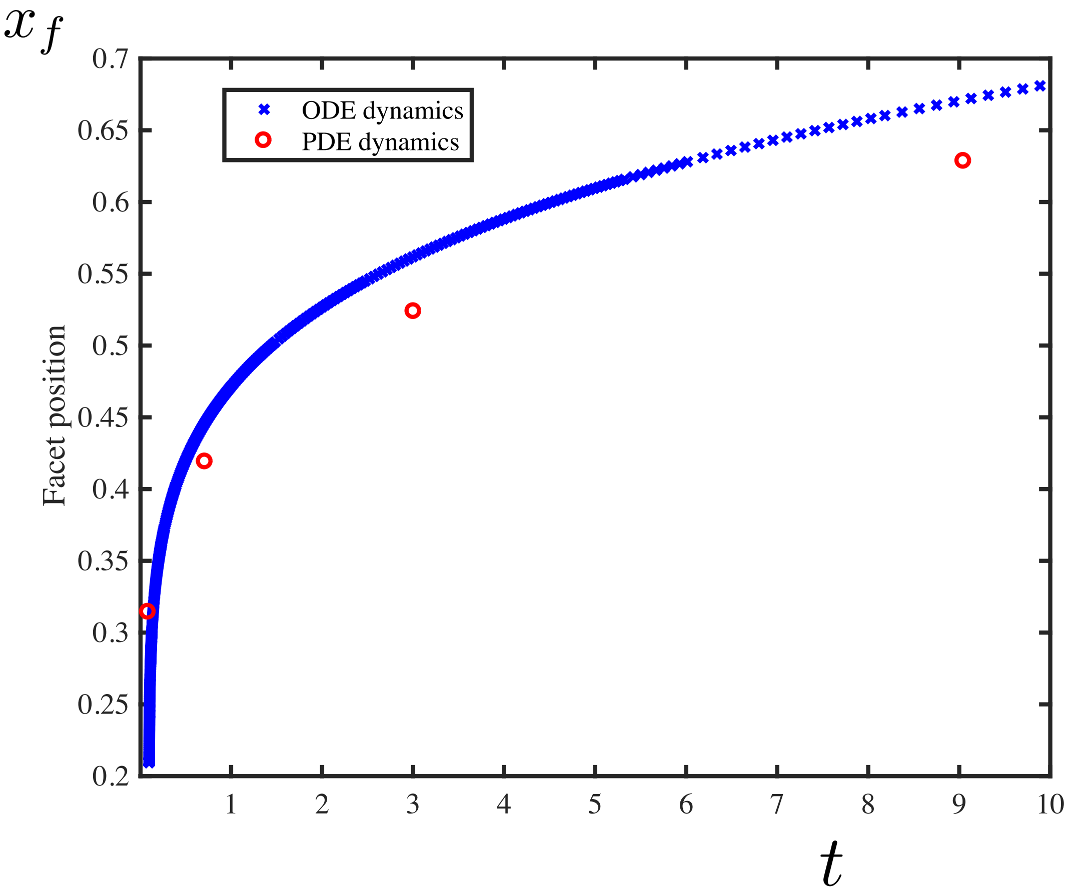
PDE (regularized):

$$\partial_t h = \partial_{xx} e^{-\partial_x\left(\frac{\partial_x h}{\sqrt{(\partial_x h)^2+\nu^2}}\right)} \; ; h_0(x) = \sin(2\pi x)$$





Numerical simulations of PDE vs ODEs (cont.)



Conclusion and Pending Issues. II.

- Gibbs-Thomson formula at step flow yields an “exponential PDE” as formal continuum limit.
- In 1+1 dimensions and without elasticity, this PDE predicts: distinct evolutions of top and bottom facets, discontinuous surface height; cf. [Giga, Giga, 2010]

- What is the rigorous continuum theory?
- What is the connection of continuum prediction to step flow?
- Effect of elasticity at continuum level?
- Refined numerics?