Three Tales of Three Scales in Epitaxial Growth:
Lecture II:
Reconciling step motion with crystal facet evolution

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"Classical" shape relaxation by surface diffusion

[Herring, 1950, 1951; Mullins, 1957]

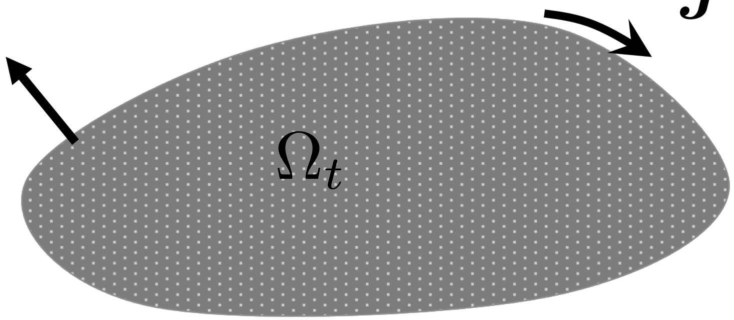
surface flux

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

diffusivity

surface chem. potential

$$\boldsymbol{J} = -\frac{D_s \rho_s}{k_B T} \nabla_\Gamma \mu$$



(const.) surface free energy/area

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

mean curvature

$\Gamma_t = \partial \Omega_t$: smooth

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

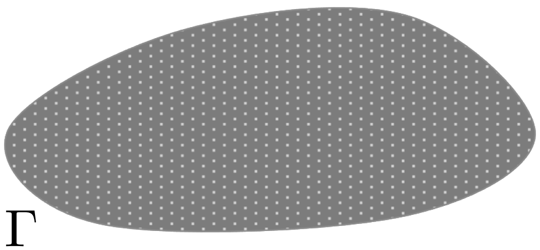
lifetime

size

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

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

On surface relaxation by the Mullins model



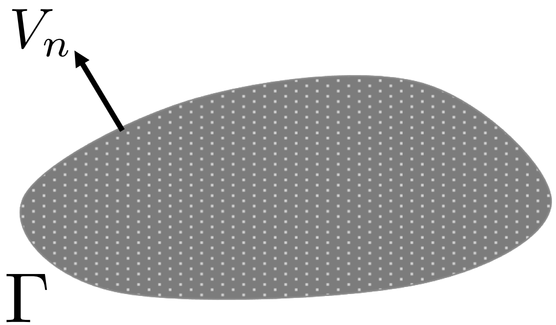
Is surface flux driven by the chemical potential or the adatom density?

Much less developed view [Mullins, 1957]: $\mathbf{J} = -D_s \nabla_\Gamma \rho$

(Gibbs-Thomson relation) $\rho = \rho_s \exp\left(\frac{\mu}{k_B T}\right)$

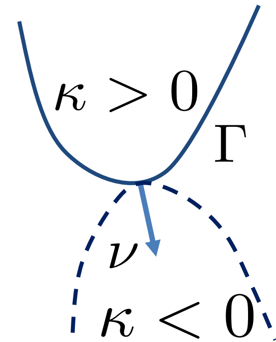
On surface relaxation by the Mullins model

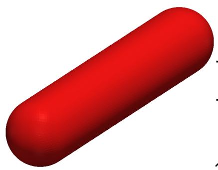
[Nichols, 1976; DM, Nurnberg, Sudoh, *in prep.*]



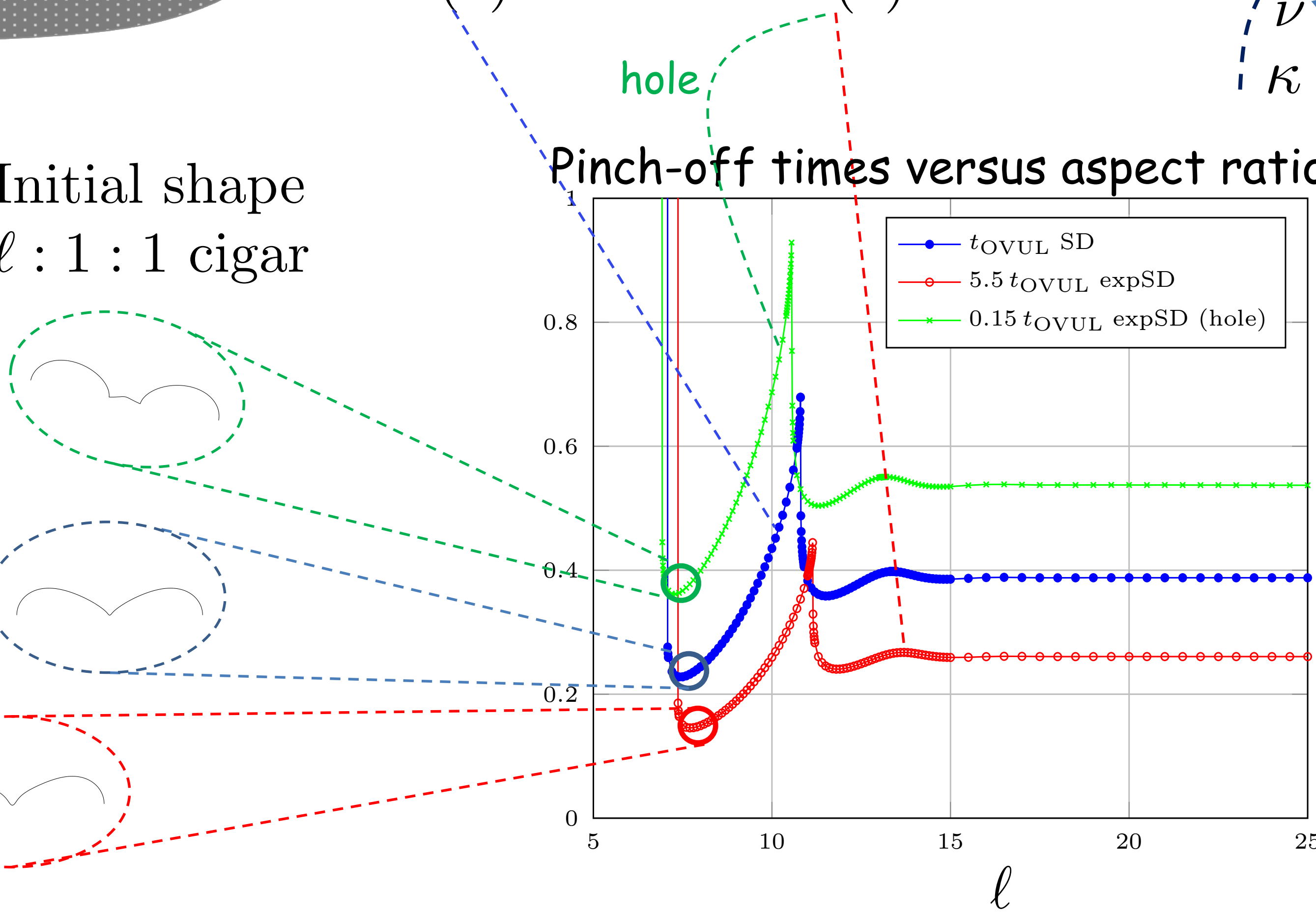
$$V_n = \nabla_\Gamma \cdot (b(\kappa)\nabla_\Gamma \kappa)$$

$b(s) = 1$ $b(s) = e^{-s}$

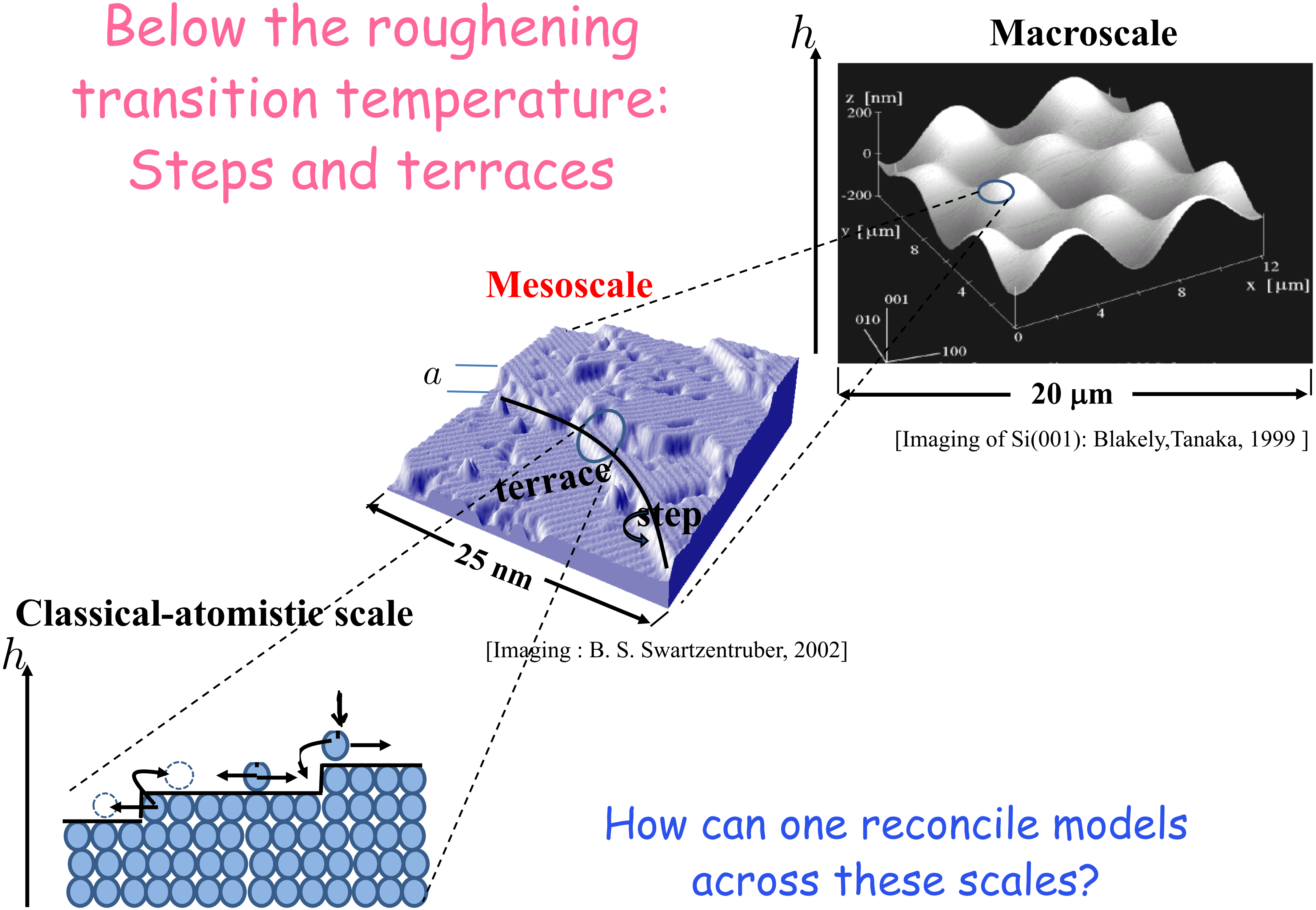




Initial shape
$\ell : 1 : 1$ cigar



Below the roughening transition temperature: Steps and terraces

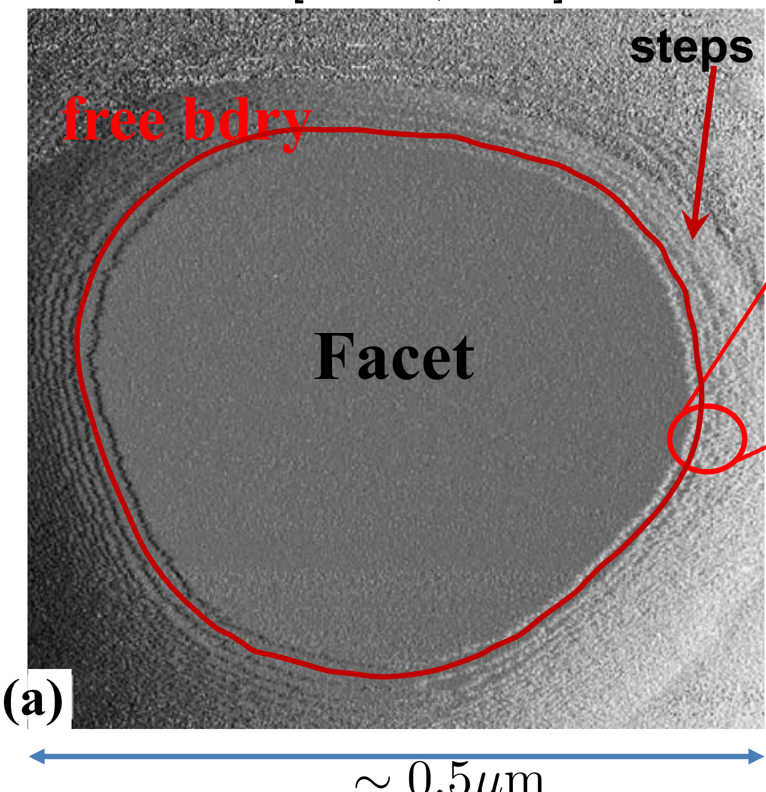


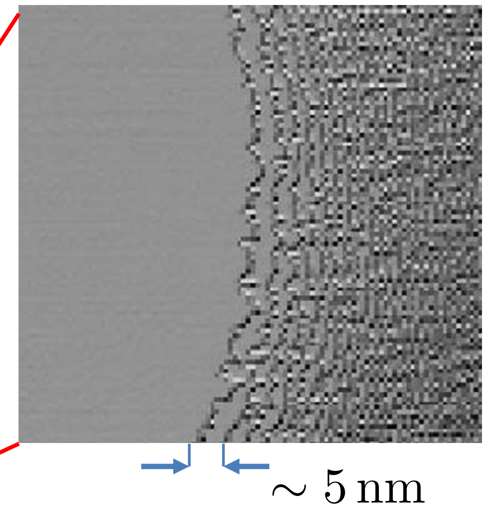
How can one reconcile models across these scales?

What is a "suitable" macroscale description?

Crystal facets (macroscopic plateaus)

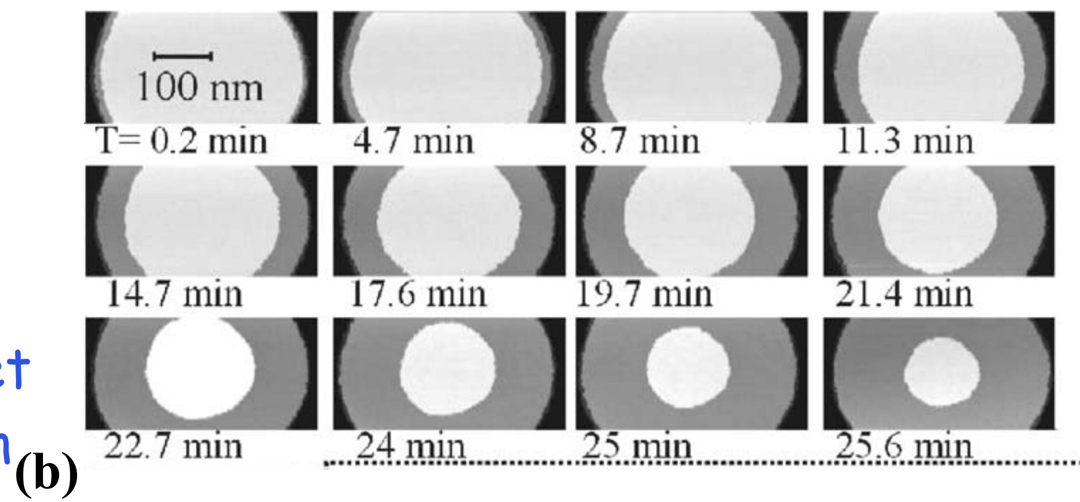
STM image: faceted Pb crystallite (top view)
[Bonzel, 2003]





How can a macroscopic description (PDE) outside facet be reconciled with step motion near facet?

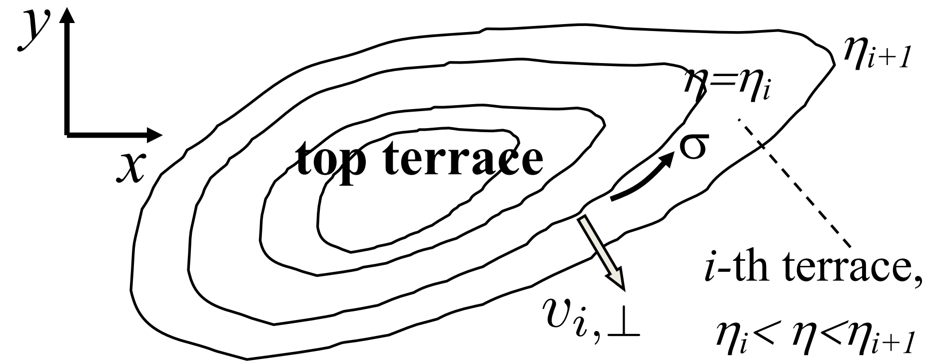
Sequence of STM images: Single-layer peeling on facet [Thurmer *et al*. 2001]



Mesoscale: Step flow: BCF model

[Burton, Cabrera, Frank, 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 :

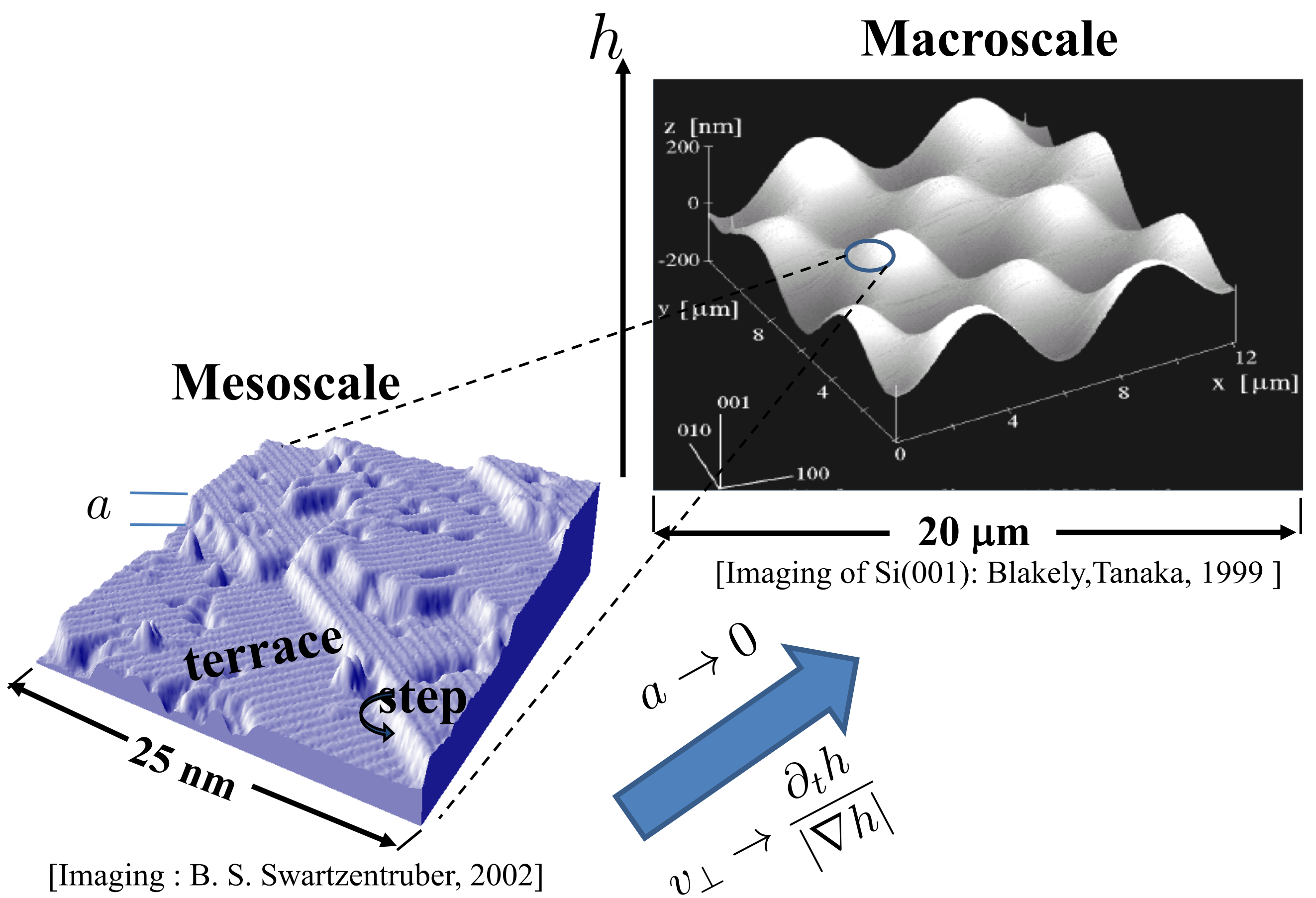
$$-J^+_{i,\perp} = q_+[\rho_i^+ - \rho_i^{\mathrm{eq}}(\sigma, t)], \; \eta = \eta_i; \; J^-_{i,\perp} = q_-[\rho_i^- - \rho_{i+1}^{\mathrm{eq}}(\sigma, t)], \; \eta = \eta_{i+1}$$

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

Gibbs-Thomson relation [Rowlinson, Widom, 1982…]

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

From step motion laws to PDEs



[**Sample of studies in physics/math. physics:** Spohn, 1993; Selke, Duxbury, 1995; Chame, Rousset, Bonzel, Villain, 1996; Israeli, Kandel, 1999; Chame, Villain, 2001]

[**Rigorous analysis:** Al Hajj Shehadeh, Kohn, Weare, 2011; Gao, Ji, Liu, Witelski, 2018]

Scope

Facets are **special** regions of the crystal surface.

We need to understand how microscale step motion influences facet evolution.

Issues:
- PDE away from facet?
- Boundary conditions at facet?

[DM, Aziz, Stone, 2005; DM, Kohn, 2006; Fok, Rosales, DM, 2008; Bonito, Nochetto, Quah, DM, 2009; DM, Nakamura, 2011; Nakamura, DM, 2013; Schneider, Nakamura, DM, 2014; Liu, Lu, DM, Marzuola, *submitted*]

Relaxation PDE in 2+1 dimensions, outside facets

[DM, Kohn, 2006]

Total step energy

$$\frac{dE_N^{\mathrm{st}}}{dt} = \sum_i \int_{step\, i} v_{i,\perp}\, \mu_i\, \mathrm{d}s \quad \overset{a \to 0}{\Longrightarrow} \quad \mu_i \to \mu = \left(\frac{\delta E}{\delta h}\right)_{L^2}$$

step veloc.

Ill-defined on facet

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: $\nabla h = 0$

Singular surface free energy

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

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

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

Flux (Fick-type law)

Tensor mobility; in **diffusion-limited** kinetics, M=1

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

mass conservation

4th-order, parabolic-like PDE for h

Generally (without linearization):

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

PDE in diffusion-limited kinetics (M=1)

By **linearized** Gibbs-Thomson relation:

$$\partial_t h(x,t) = C\Delta\left[-\mathrm{div}\left(\frac{\nabla h}{|\nabla h|} + g|\nabla h|\nabla h\right)\right]$$

singular at facet

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

What is the meaning of this evolution equation (in continuum-scale framework) in presence of facets?

[**Aspects of analysis:** Kobayashi, Giga, 1999; Spohn, 1993; Odisharia, Thesis, 2006; Kashima, 2004; Giga, Giga, 2010; Giga, Kohn, 2011…]

PDE: Extended-gradient formalism,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

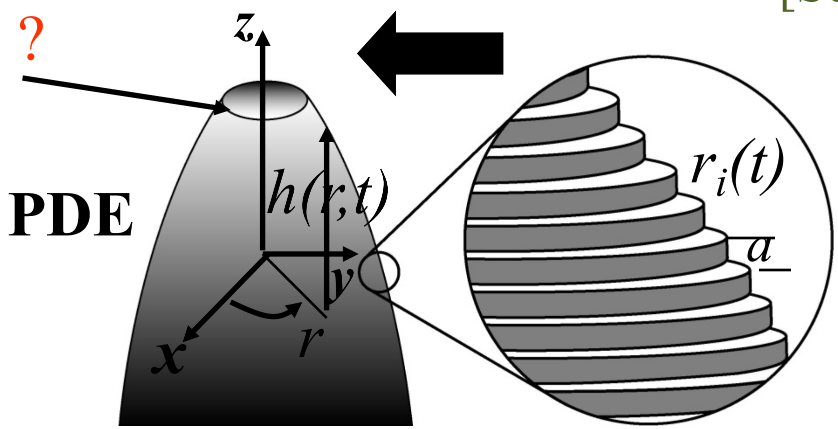
"Natural" boundary conditions at facet edges follow.

What should the above rule amount to, practically?

Suppose the facet is smoothed out 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.

Diffusion-limited kinetics: Radial geometry

[Schneider, Nakamura, DM, 2014]



PDE:

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

H^{-1} gradient flow

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

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

Discrete scheme for steps:

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

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

Linearized Gibbs-Thomson rel.

$$\mu_i = \frac{a^3 g_1}{r_i} + \frac{a^3}{2\pi r_i} g_3 \frac{\partial}{\partial r_i}[V(r_i, r_{i+1}) + V(r_i, r_{i-1})]$$

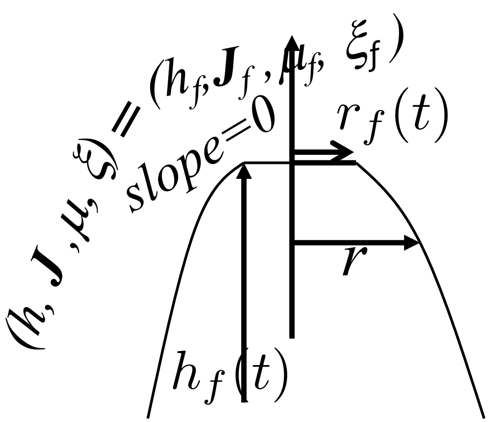
Step curvature

Nearest-neighbor, force-dipole step-step interactions

Free-boundary approach: Boundary conditions

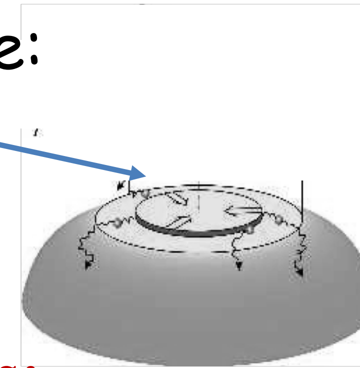
Natural BC's in radial setting

- 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



Alternative:

Collapse times t_n



Keep

Replace by jumps:

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

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

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

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

t_n: time of n-th step collapse

In close agreement with step simulations;

$$Q(t) \approx \text{const.}, \qquad n \gg 1$$

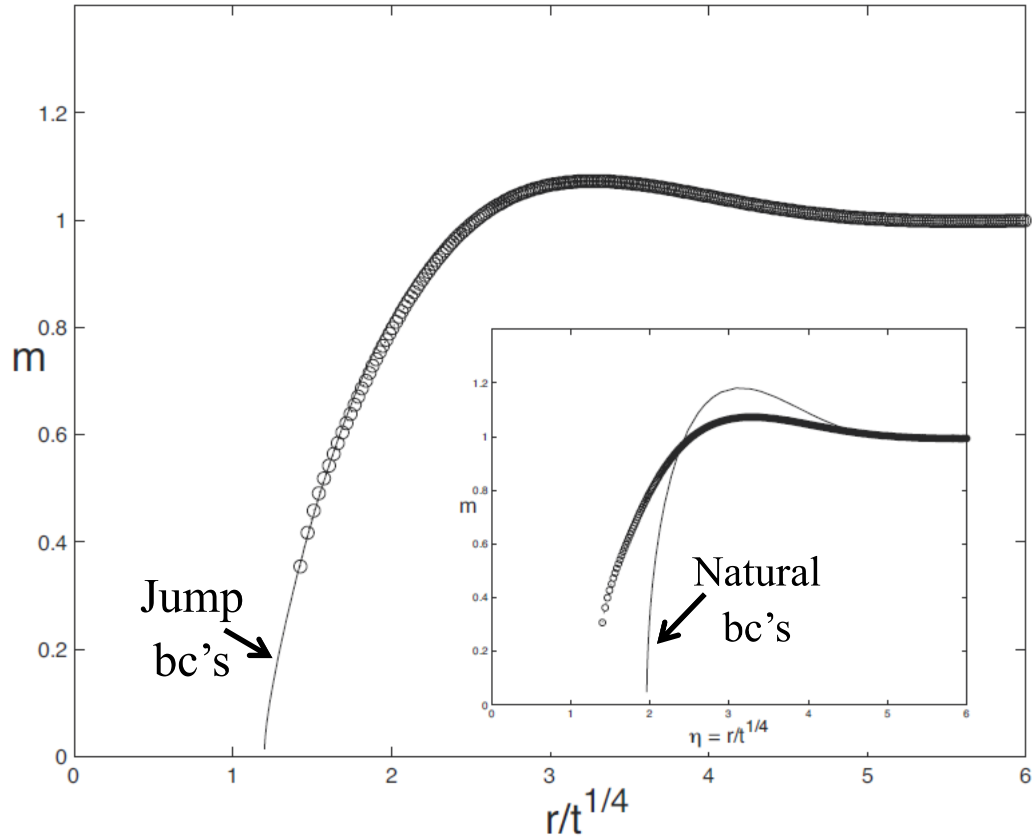
[Schneider, Nakamura, DM, 2014]

Numerics: Conical initial data; self-similar regime

Discrete slopes behave as self-similar for long times

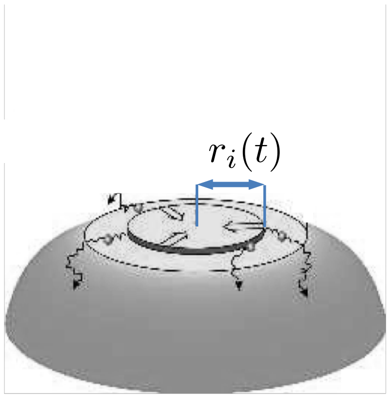
Ansatz: $m(r,t) \approx \mathfrak{M}(rt^{-1/4})$

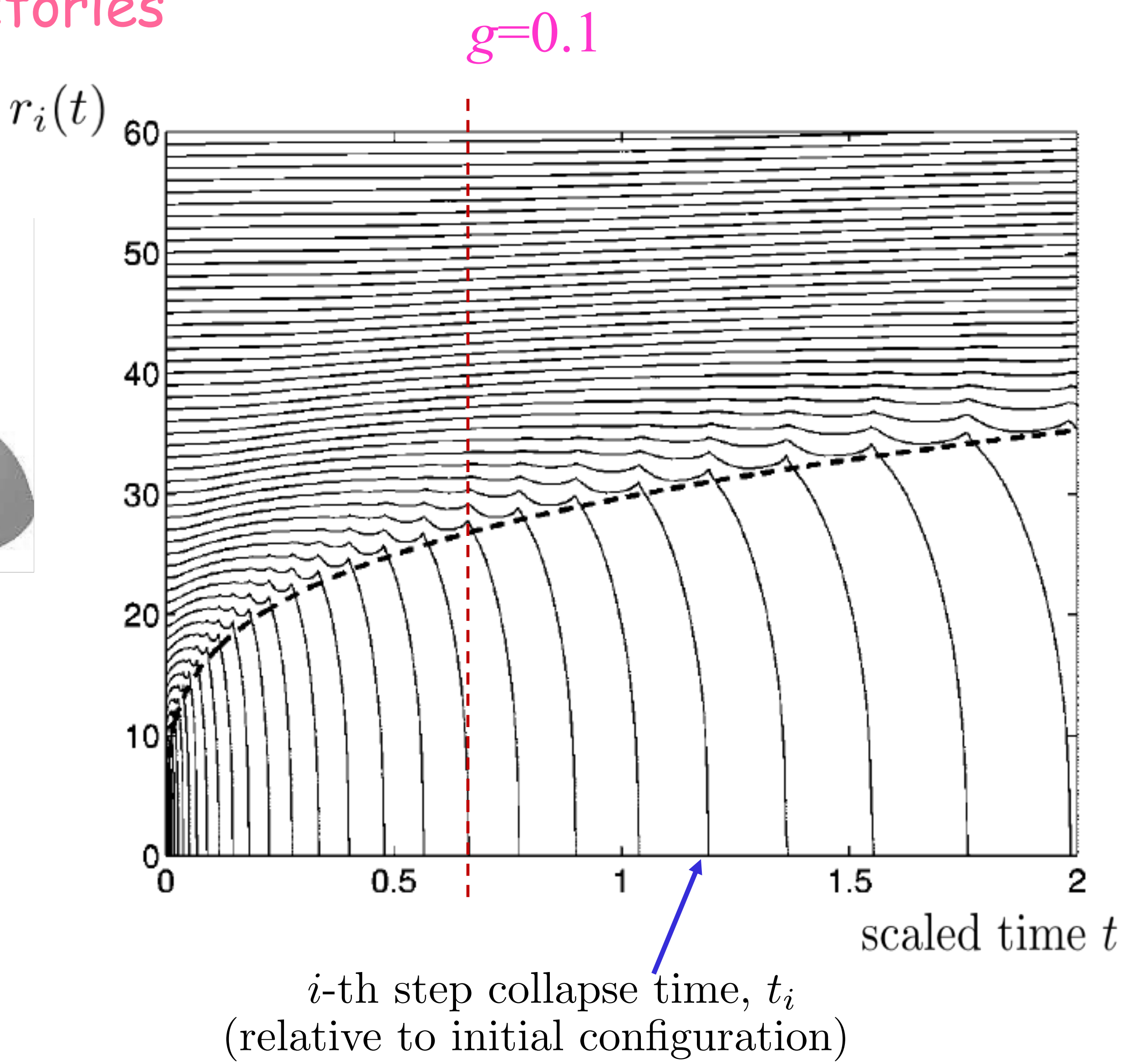
Rel. step interaction strength: *g*=0.1



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

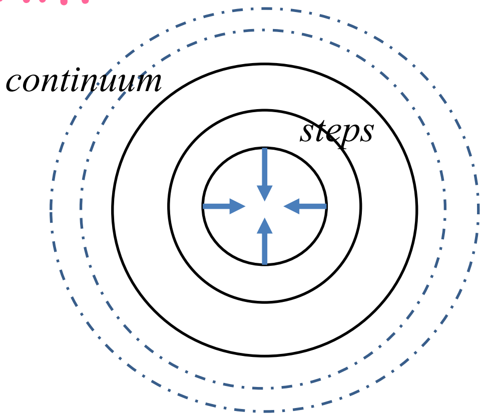
Step trajectories





"Hybrid" iterative scheme: Algorithm

Top view



1. Compute slope profile 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: $n_0 = 0 \; , \; n_* \geq 1 \; ; \; \tilde{t}_0 = 0$

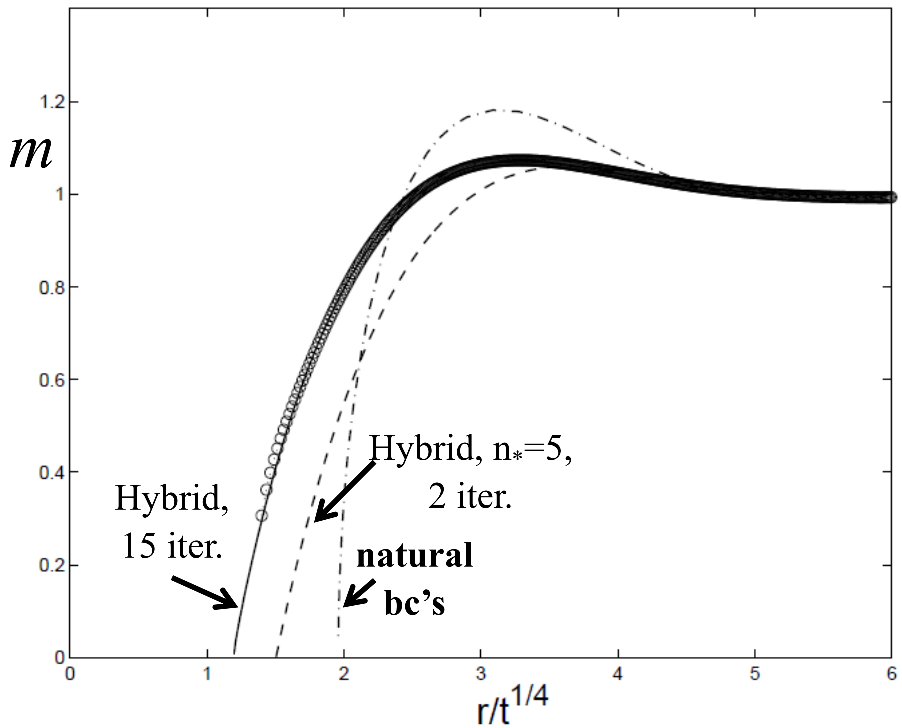
3. Re-compute slope using jump conditions at: $t = t_{n_*}$

4. Go to **2**, and **iterate** (advancing time).

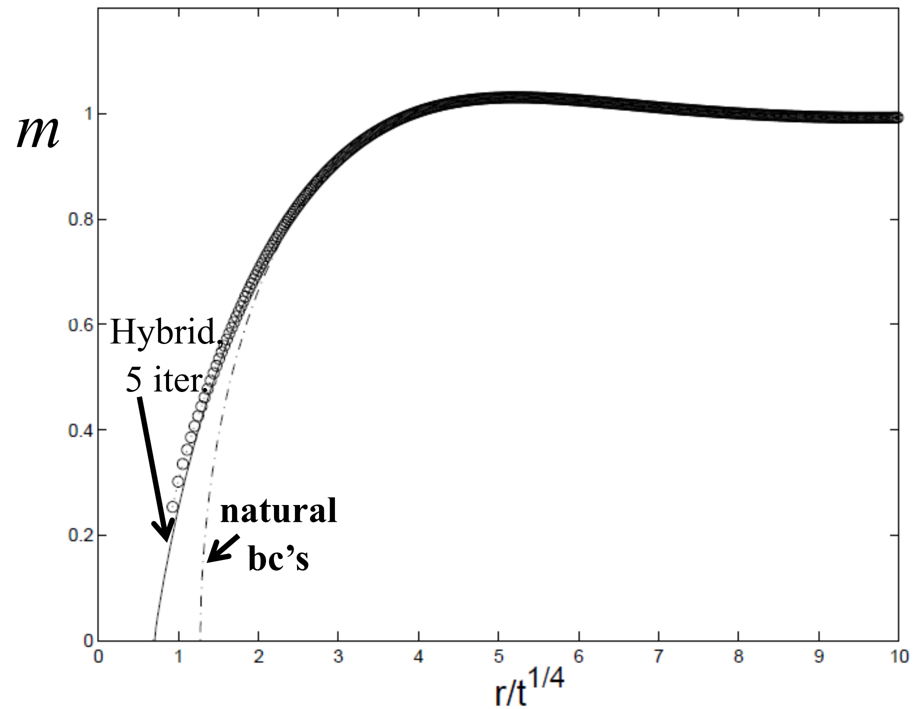
[Schneider, Nakamura, DM, 2014]

Numerics (conical initial data)

g=0.1



g=1



Open questions:

Can one *derive* jump conditions from step motion?

How about other kinetic regimes? Non-radial geometry?

PDE from full Gibbs-Thomson relation for steps

[Liu, Lu, DM, Marzuola, *subm.*]

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

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

PDE plausibly comes from scaling limit of atomistic dynamics

[Marzuola, Weare (2013)]

Open issue: Rigorous formulation of appropriate gradient flow

What plausible predictions for facets can be made by this PDE (in a full continuum-scale framework) ?

Reduction to 1+1 dimensions; **periodic** profile

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

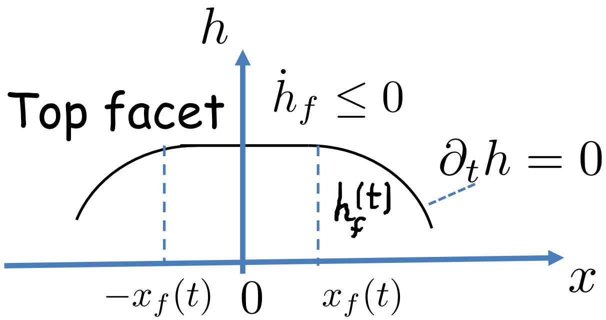
Neglect of $|h_x|h_x$ term

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

Note: If $\partial_x h \neq 0$ then $\partial_t h = 0$.

Claim: BC's at facet:
- 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; $h(-x,t) = h(x,t)$.
- Facet has zero slope; $\partial_x h = 0$.
- $\xi(p) = p/|p|$ (p: slope) is extended onto facet as odd function on $\mathbb{R}$; set $\tilde{\xi}(x,t) = \xi(\partial_x h)$.
- Mass flux $J(x,t)$ is extended onto facet; and $J(x,t) = J(-x,t)$.

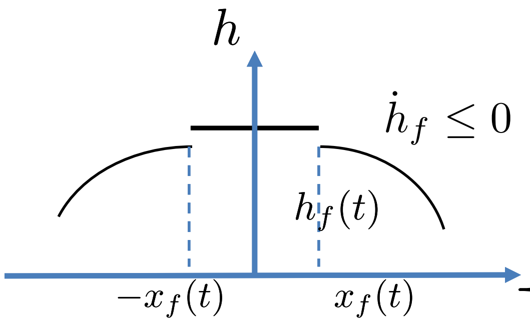
PDE structure: $\boxed{\partial_t h = -\partial_x J,\;\; J = -\partial_x e^{\mu},\;\; \mu = -\partial_x \tilde{\xi};}$ $h(x,0) = h_0(x)$

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

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

Apply:
Mass conservation: $\dot{x}_f[h_0(x_f) - h_f] = \dot{h}_f x_f$
Continuity of $\tilde{\xi}(\cdot,t)$, $\mu(\cdot,t) \Rightarrow C_2(t) = 1 - x_f^2\dot{h}_f/2$, and extra relation between x_f, $\dot{h}_f$.

Free-boundary approach: ODEs



ODE system for (x_f, h_f), **top** facet $(\dot{h}_f \leq 0)$:

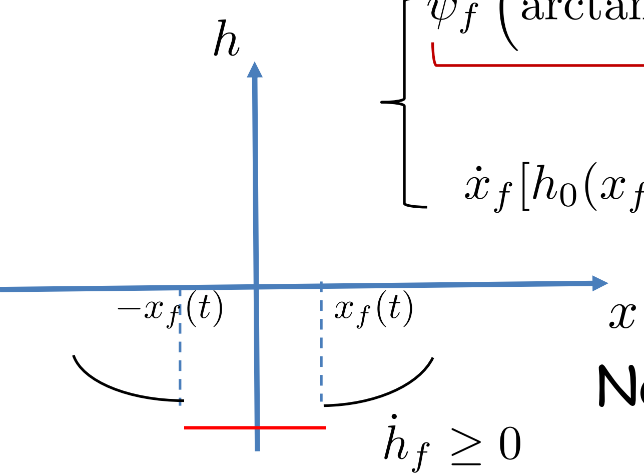
$$\begin{cases} 2\sqrt{1+X_f^2}\,\ln\left(\sqrt{1+X_f^2}+X_f\right) - 2X_f = \sqrt{\dfrac{|\dot{h}_f|}{2}}\ ; \quad X_f := x_f\sqrt{\dfrac{|\dot{h}_f|}{2}} \\[2ex] \dot{x}_f[h_0(x_f) - h_f] = \dot{h}_f\, x_f \end{cases}$$

The top facet **expands**

The bottom facet behaves **differently:**

ODE system for (x_f, h_f), **bottom** facet $(\dot{h}_f \geq 0)$:

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



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

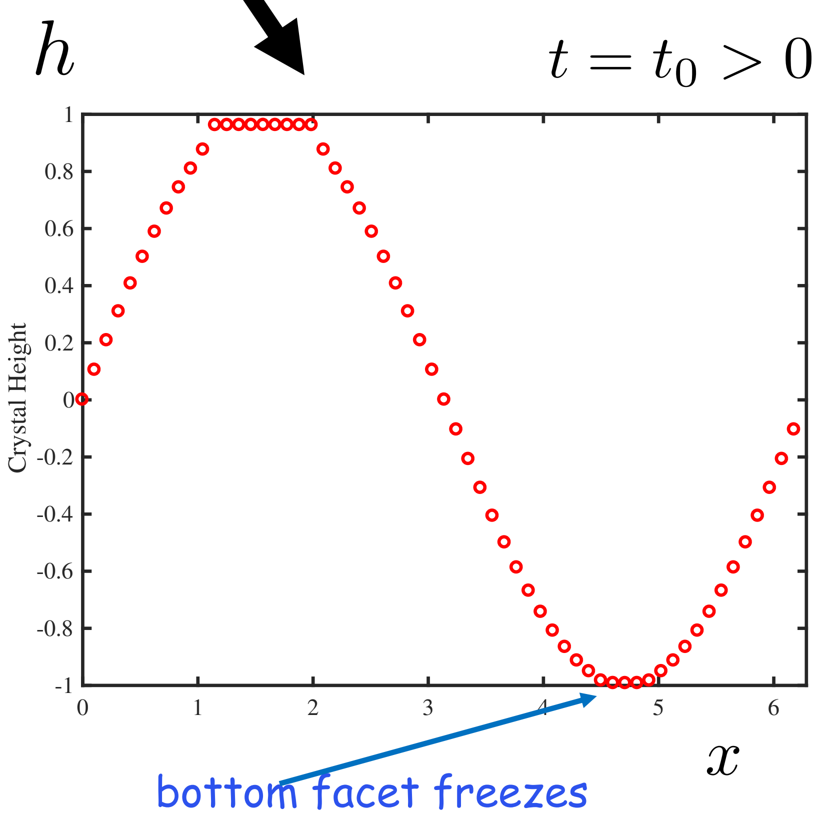
Numerical simulations of PDE and ODEs solutions

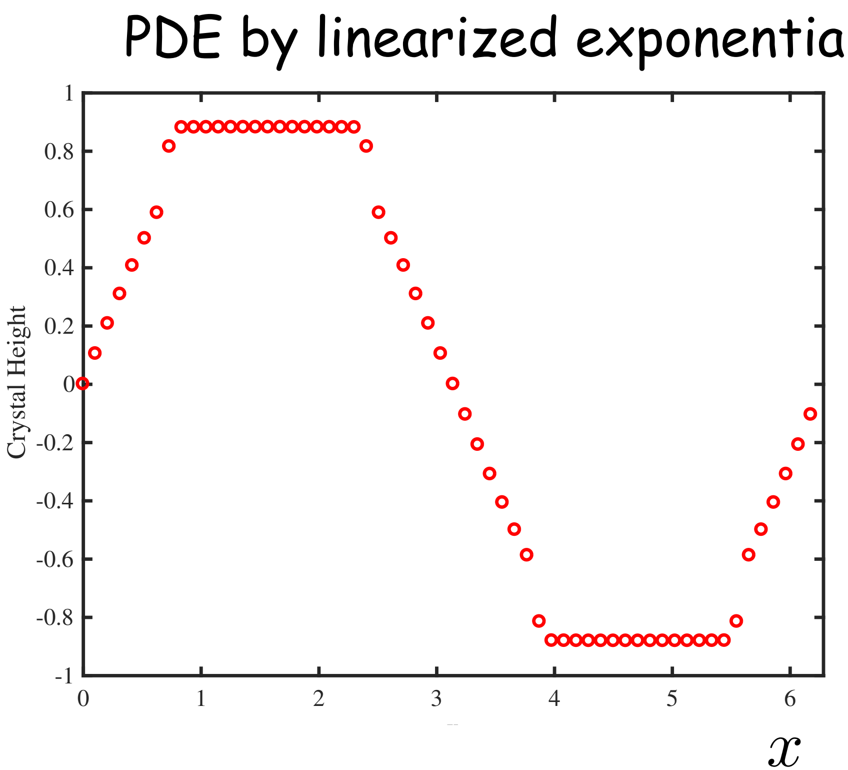
[Liu, Lu, DM, Marzuola, *subm.*]

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

Exp. PDE (regularized):

$$\partial_t h = \partial_{xx} e^{-\partial_x\left(\frac{\partial_x h}{\sqrt{(\partial_x h)^2+\nu^2}}\right)} \; ; \quad h(x,t=0) = \sin(2\pi x)$$

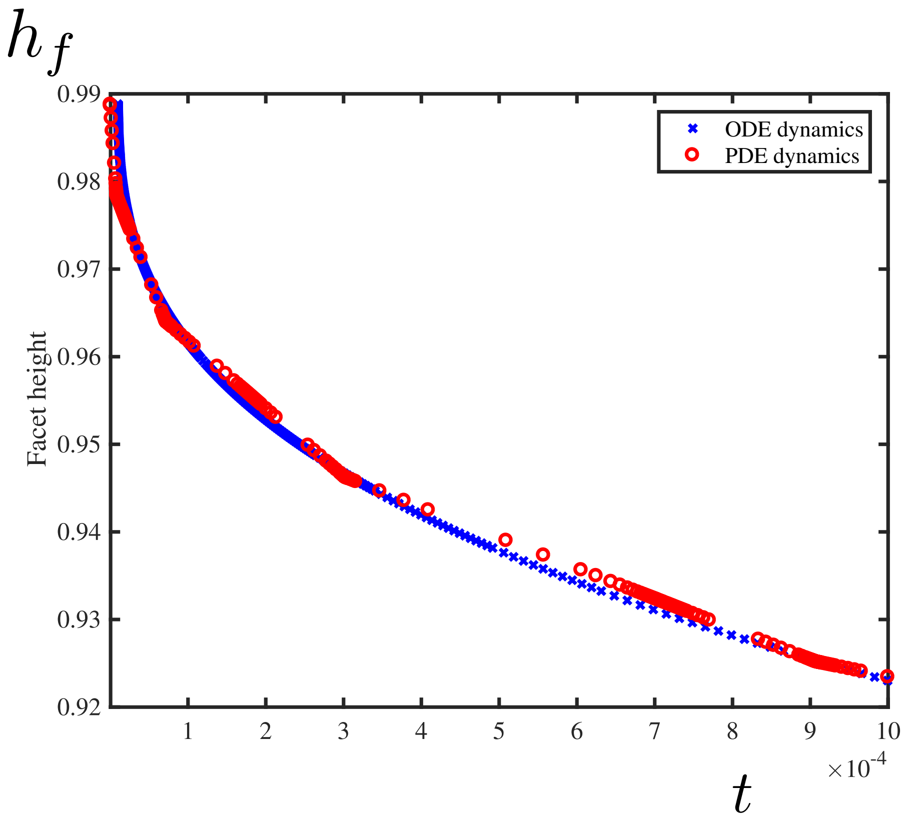




Numerical simulations of PDE and ODE solutions (cont.)

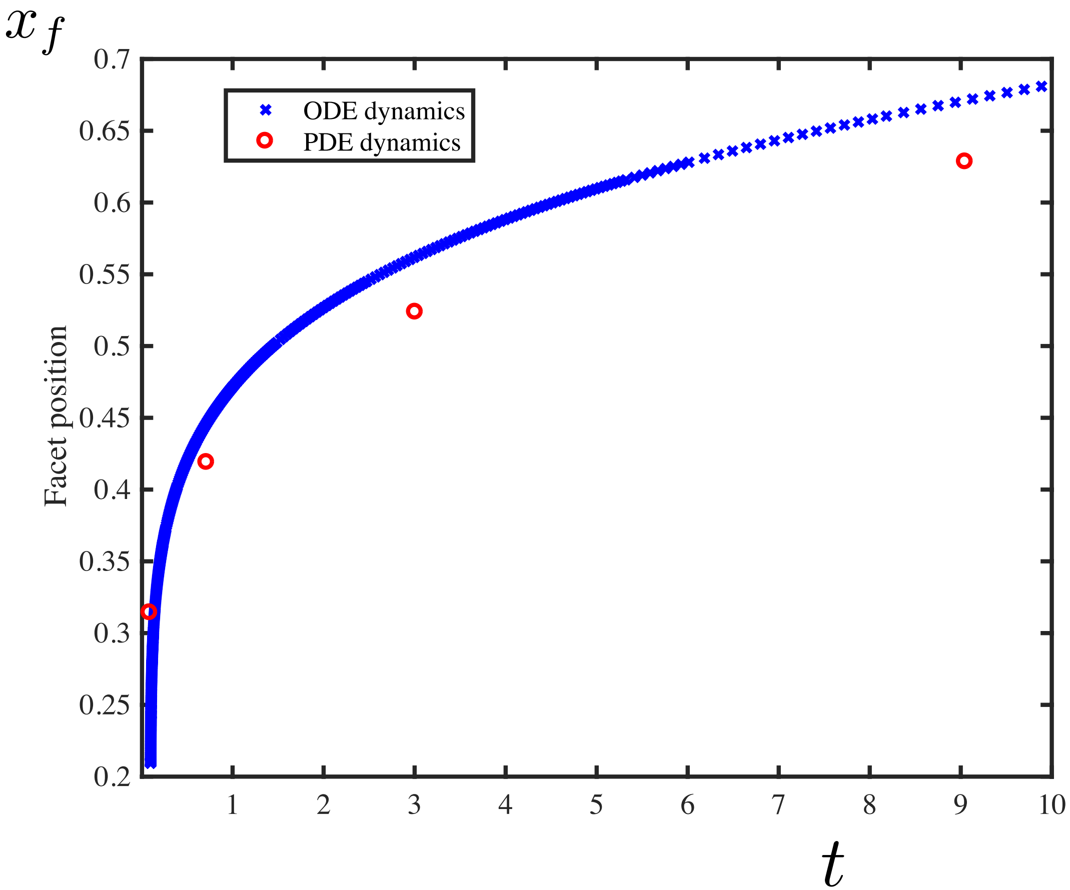
[Liu, Lu, DM, Marzuola, *subm.*]

Facet height



Open question: How does this prediction compare to step motion?

Numerical simulations of PDE vs ODEs (cont.)



Conclusion and Outlook

- Boundary conditions for PDE at facets need step microstructure. Proposal: jump discontinuities of thermodynamic variables.

  Can the jump conditions emerge from limits of step flow?

- 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).

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

  Does the hybrid scheme really converge? Why?

- Full Gibbs-Thomson formula in step flow model yields an "exponential PDE" as formal continuum limit. This expresses top-bottom asymmetry in relaxation of height profile.

  Connection of continuum prediction to (discrete) step flow?