From atoms to macroscopic laws: The case of epitaxial growth

Dionisios Margetis[*]
Department of Mathematics,
and Institute for Physical Science & Technology (IPST),
and Ctr. for Scientific Computation And Math. Modeling (CSCAMM)

Univ. of Maryland at College Park, USA

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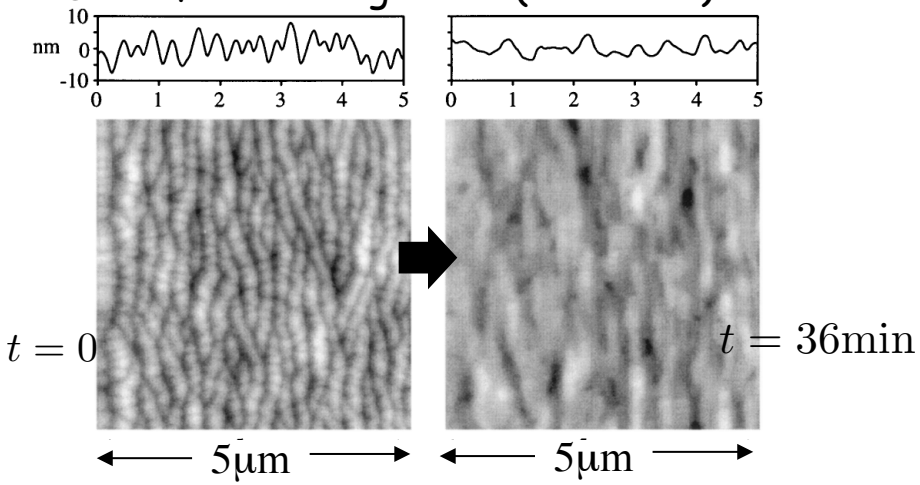
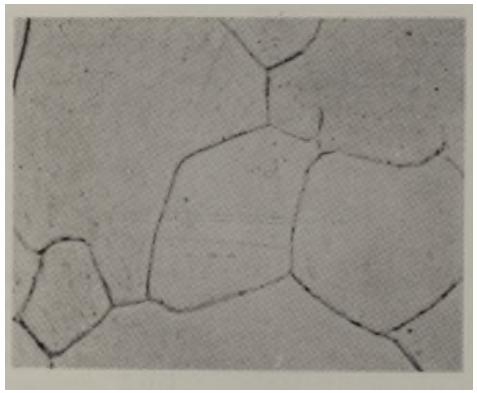
Crystal surfaces out of equilibrium: A sample

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



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

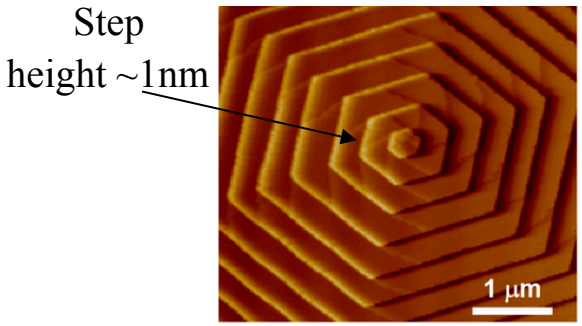
Thermal grooving in Ag (temp. T=920° C)



[Chalmers, King, Shuttleworth, 1948]

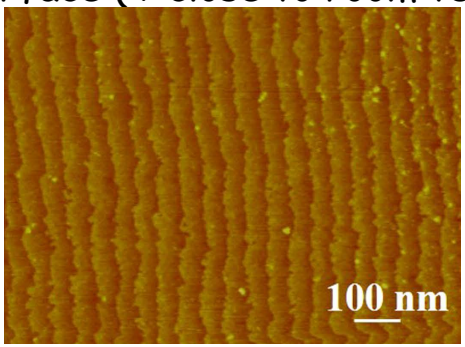
Goal: To model surface morphological evolution

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



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

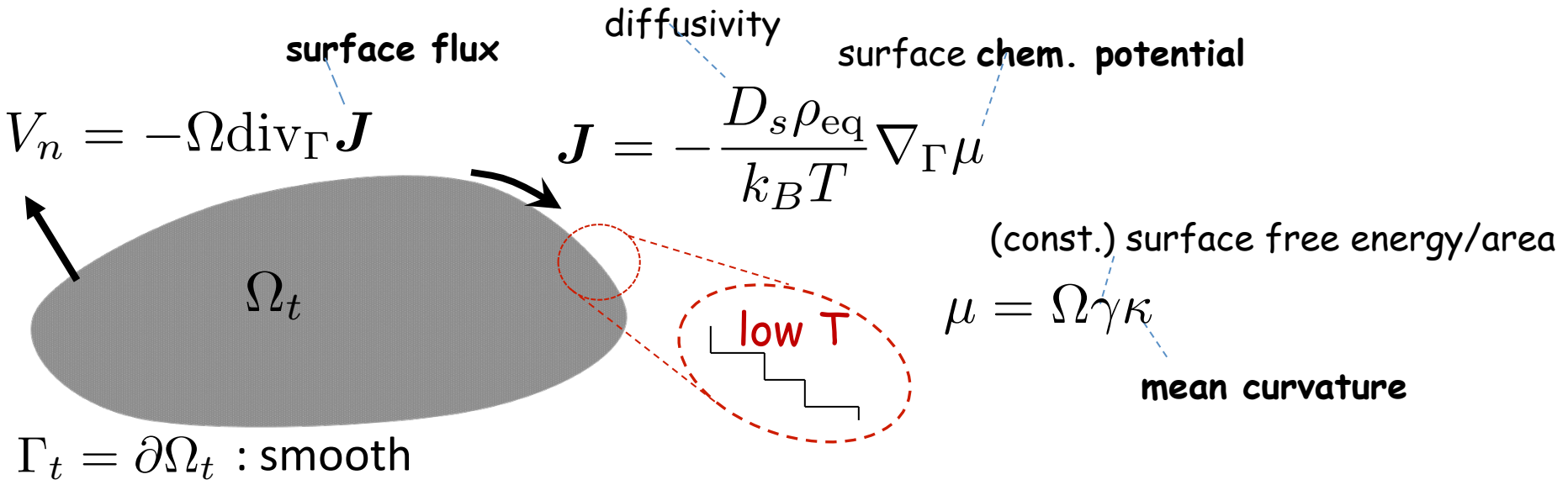
Atomic step formation on sapphire
surface (T close to room temp.)



[Wang, Guo, Xie, Pan, 2018]

"Classical" shape relaxation by surface diffusion

[Herring, 1950, 1951; Mullins, 1957]



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

lifetime; size

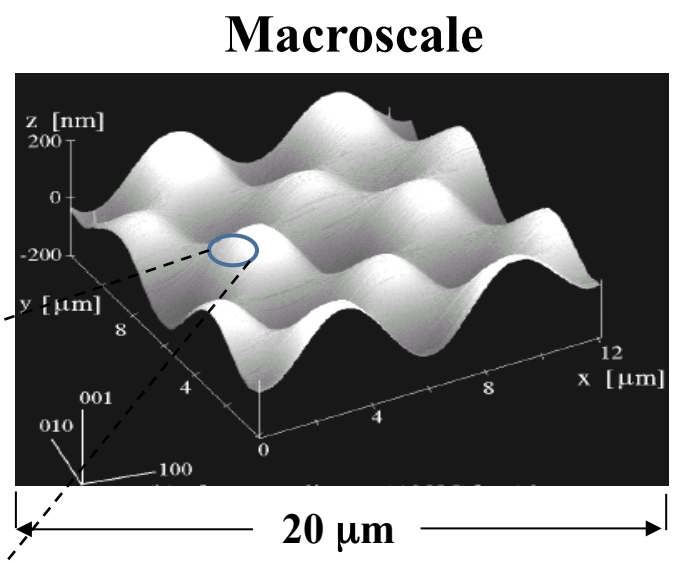
$$c(T) = CT/D_s(T)$$

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

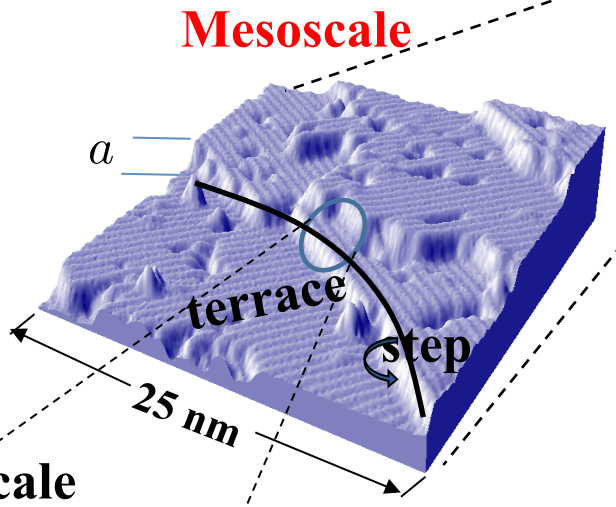
Making smaller yet stable structures implies using lower temperatures.

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

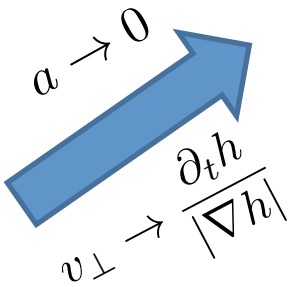
Below the roughening transition temperature: Steps and terraces



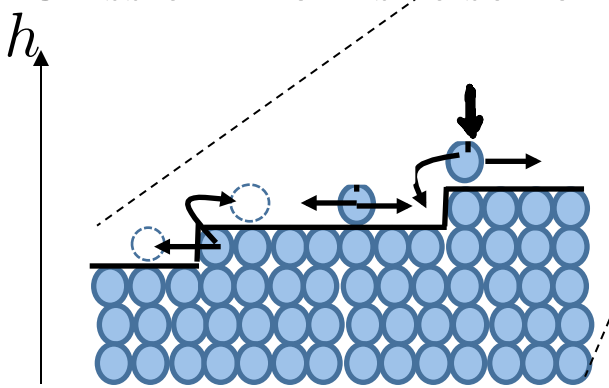
[Imaging of Si(001): Blakely,Tanaka, 1999]



[Imaging : B. S. Swartzentruber, 2002]



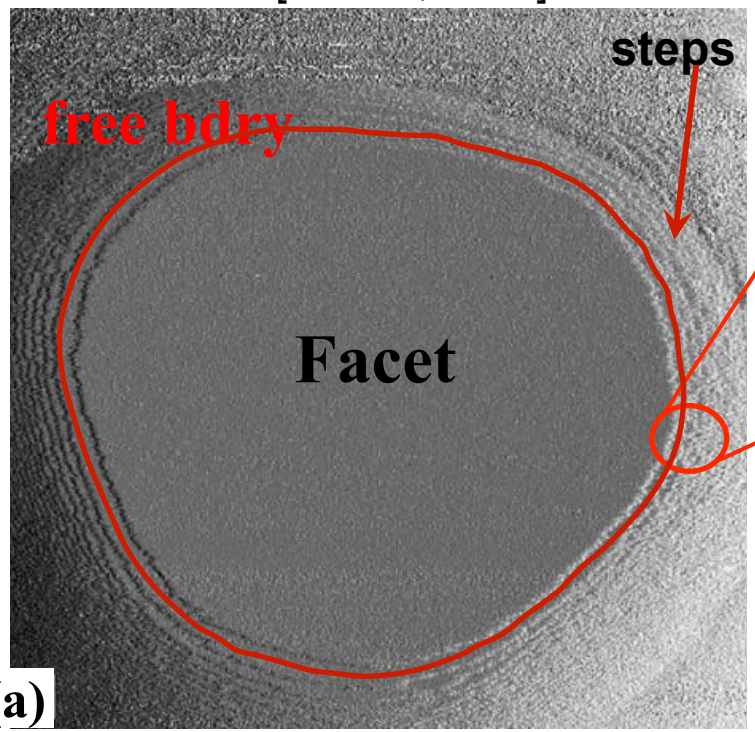
(Normal) Step velocity

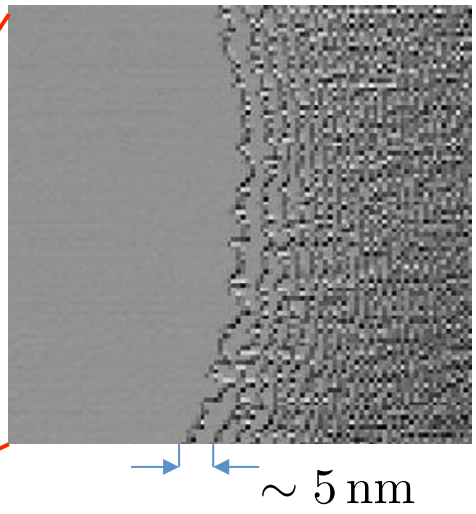


How can one reconcile models across these scales?
What is a "suitable" macroscale description?

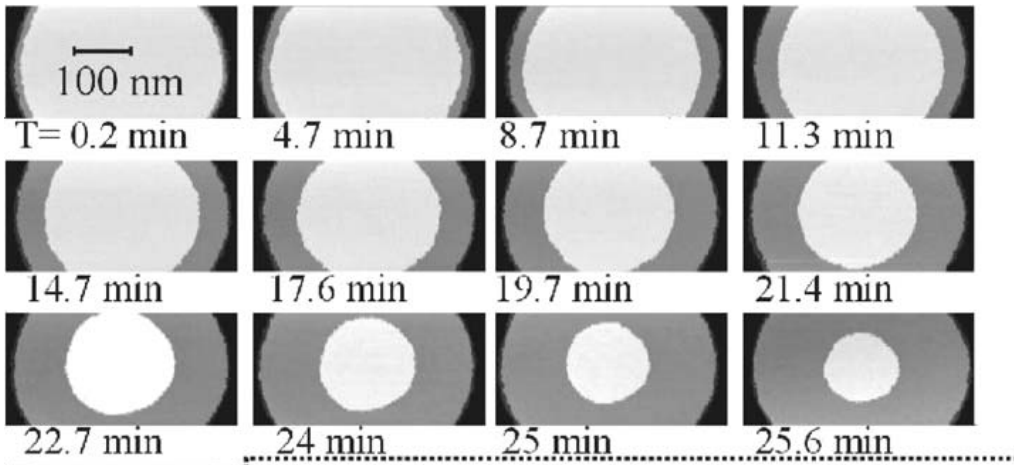
Crystal facets (macroscopic plateaus)

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





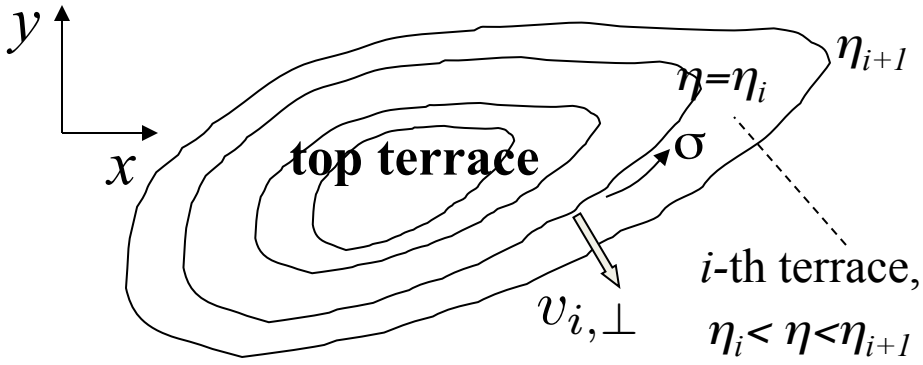
Sequence of STM images: Single-layer peeling
on facet [Thurmer *et al*. 2001]



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

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 :

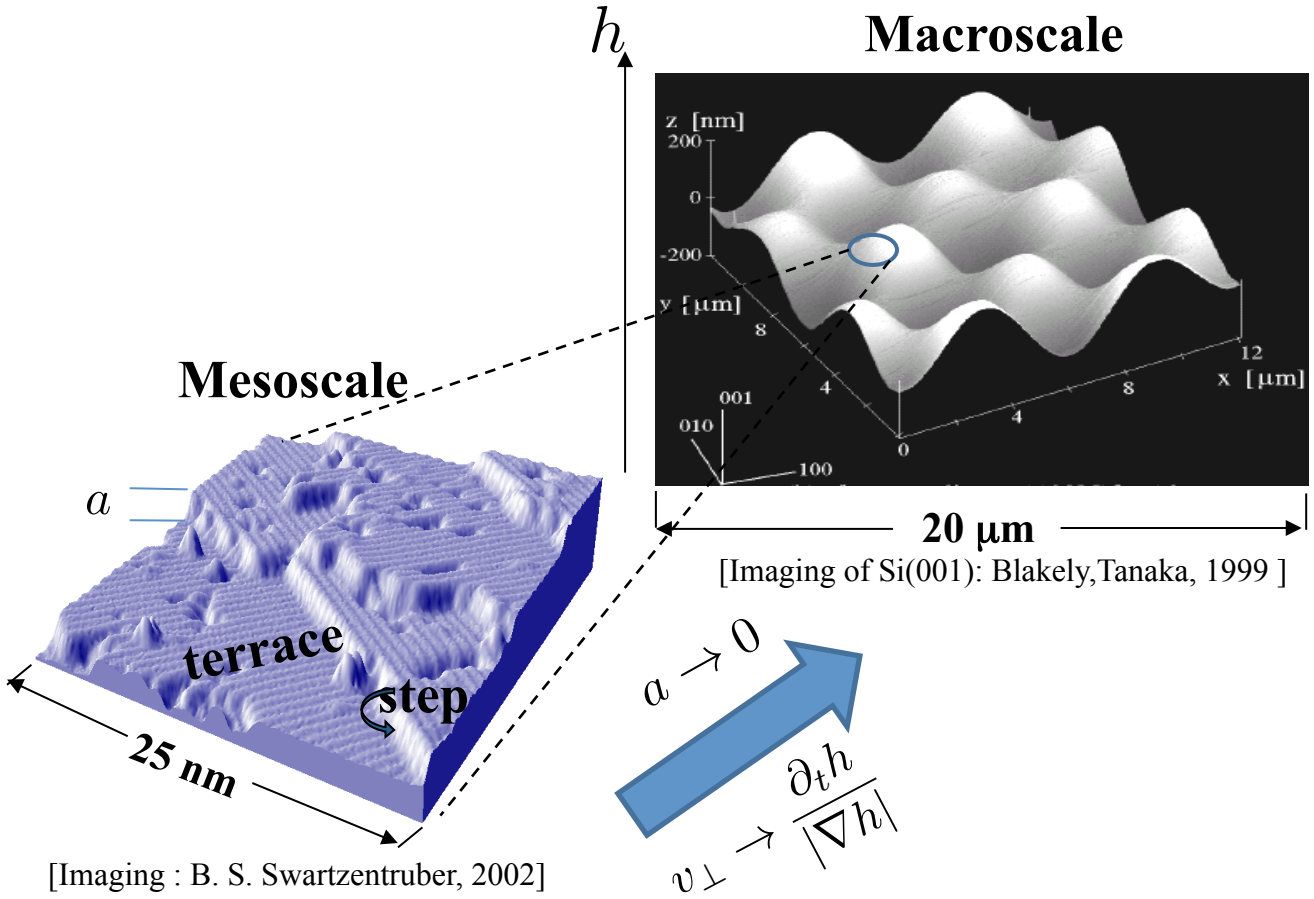
$$-J^+_{i,\perp} = q_+[\rho_i^+ - \rho_i^{\rm eq}(\sigma,t)], \;\; \eta = \eta_i; \;\; J^-_{i,\perp} = q_-[\rho_i^- - \rho_{i+1}^{\rm eq}(\sigma,t)], \;\; \eta = \eta_{i+1}$$

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

"Gibbs-Thomson relation"
[Rowlinson, Widom, 1982...]

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

I. 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

$$\frac{dE_N^{\mathrm{st}}}{dt} = \sum_i \int_{step\, i} v_{i,\perp}\, \mu_i \, \mathrm{d}s$$

step veloc.

$a \to 0$

Ill-defined on facet

$$\Longrightarrow \quad \mu_i \to \mu = \left(\frac{\delta E}{\delta h}\right)_{L^2}$$

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;

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

at step (linearization)

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

Flux (Fick-type law)

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

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

mass conservation

4^{th}-order, parabolic-like PDE for h

Gradient flow of $E[h]$

Generally (without linearization):

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

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?

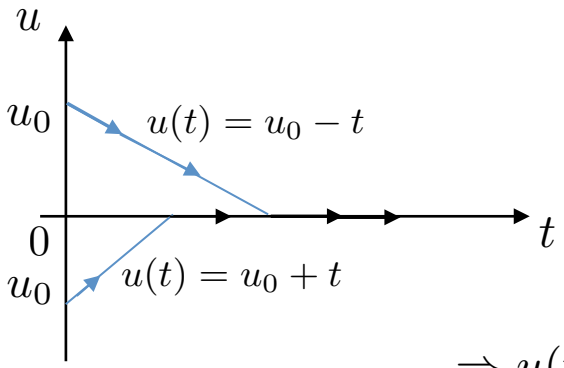
[**Aspects of analysis:** Kobayashi, Giga, 1999; Spohn, 1993; Odisharia, Thesis, 2006; Kashima, 2004; Giga, Giga, 2010; Giga, Kohn, 2011…]

Digression: ODE (toy) model

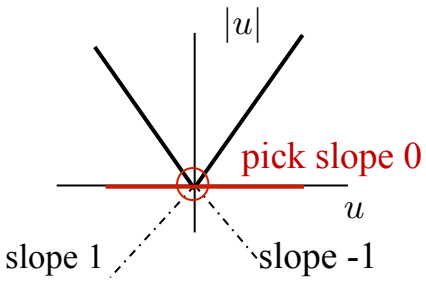
Find the continuous solution to ODE:

$$\frac{\mathrm{d}u(t)}{\mathrm{d}t} = -\underbrace{\frac{u(t)}{|u(t)|}}_{=\left(\frac{\delta}{\delta u}\right)|u| \text{ if } u \neq 0} \mathrm{sgn}(u(t))\,; \quad u(0) = u_0$$

(What happens if $u = 0$?)



Define $\dfrac{\mathrm{d}u}{\mathrm{d}t} = 0$ 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

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

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

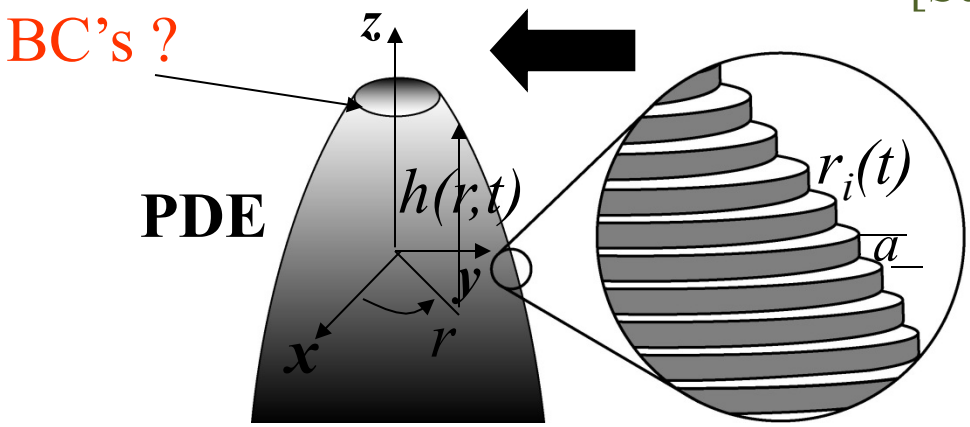
"Natural" boundary conditions at facet edges follow.

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

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

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

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.

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

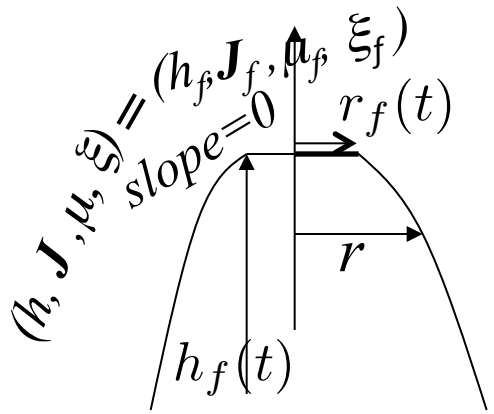
Step curvature

Nearest-neighbor, force-dipole step-step interactions

Free-boundary approach: Boundary conditions

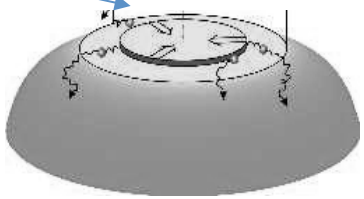
Natural BC's in radial setting

- 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:

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

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

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

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

time of n-th step collapse

In close agreement with step simulations;

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

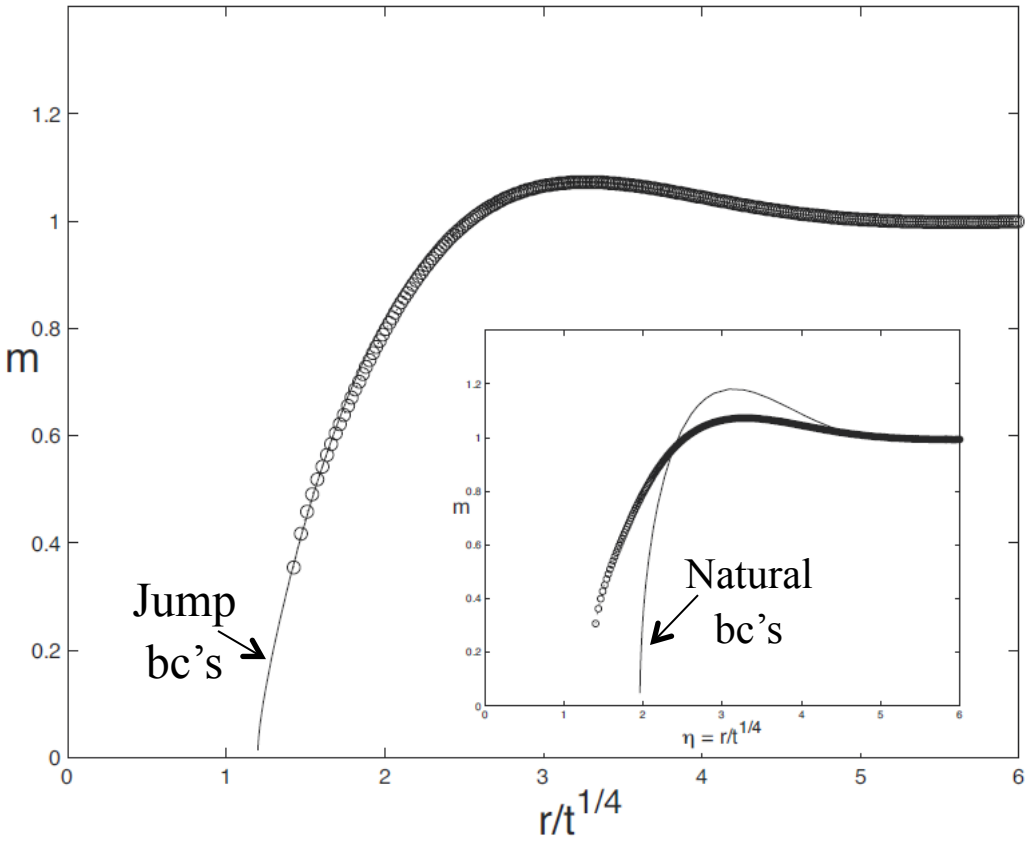
[Schneider, Nakamura, DM, 2014]

Numerics: Conical initial data; self-similar regime

Discrete slopes behave as self-similar for long times

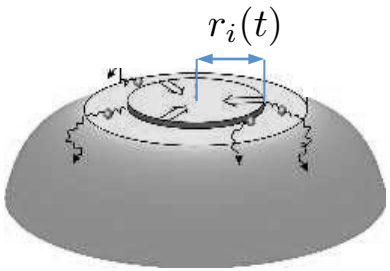
Ansatz: $m(r,t) \approx \mathfrak{M}(rt^{-1/4})$

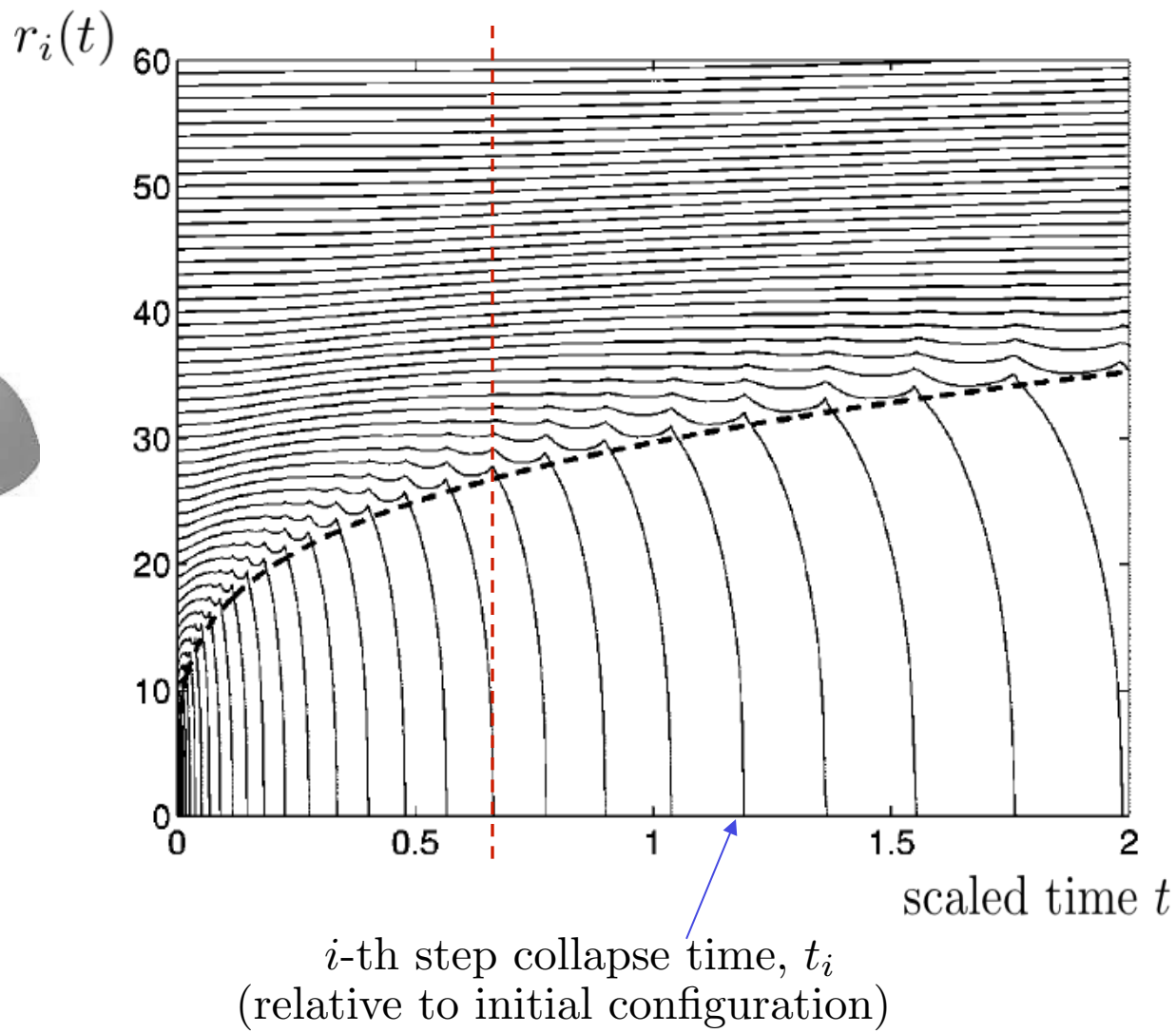
Rel. step interaction strength: g=0.1



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

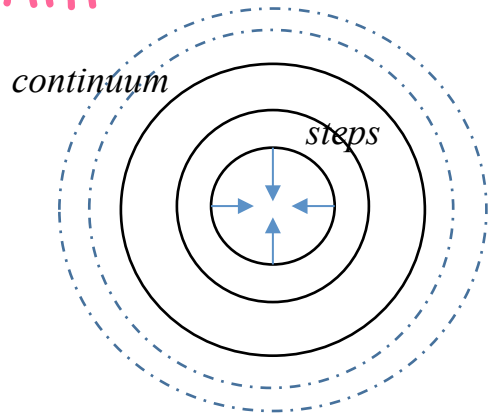
Step trajectories





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

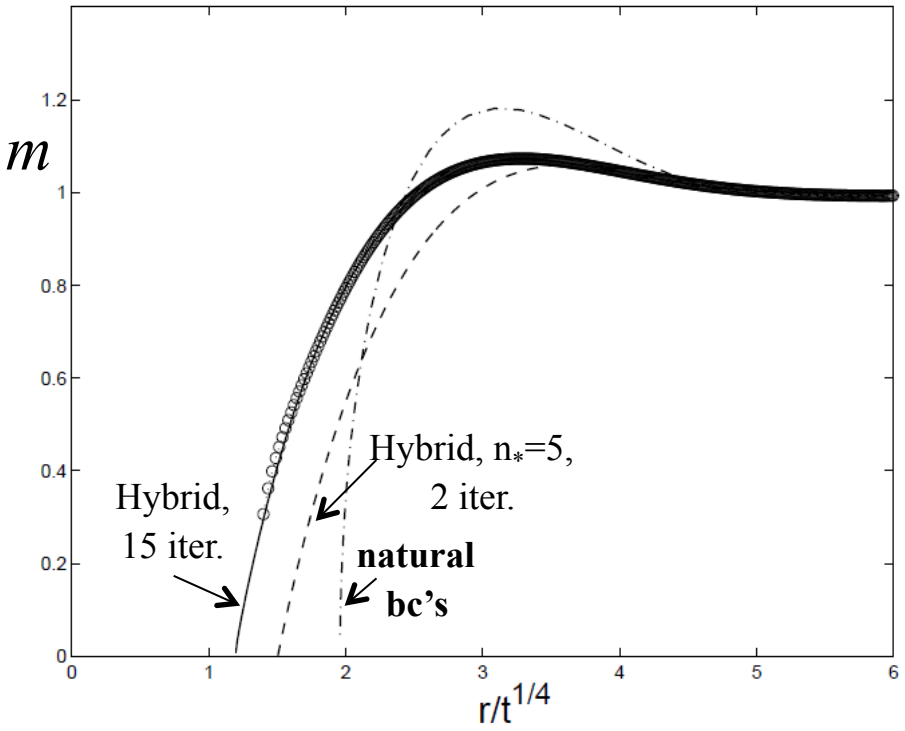
3. Re-compute slope using jump conditions at: $t = t_{n_*}$

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

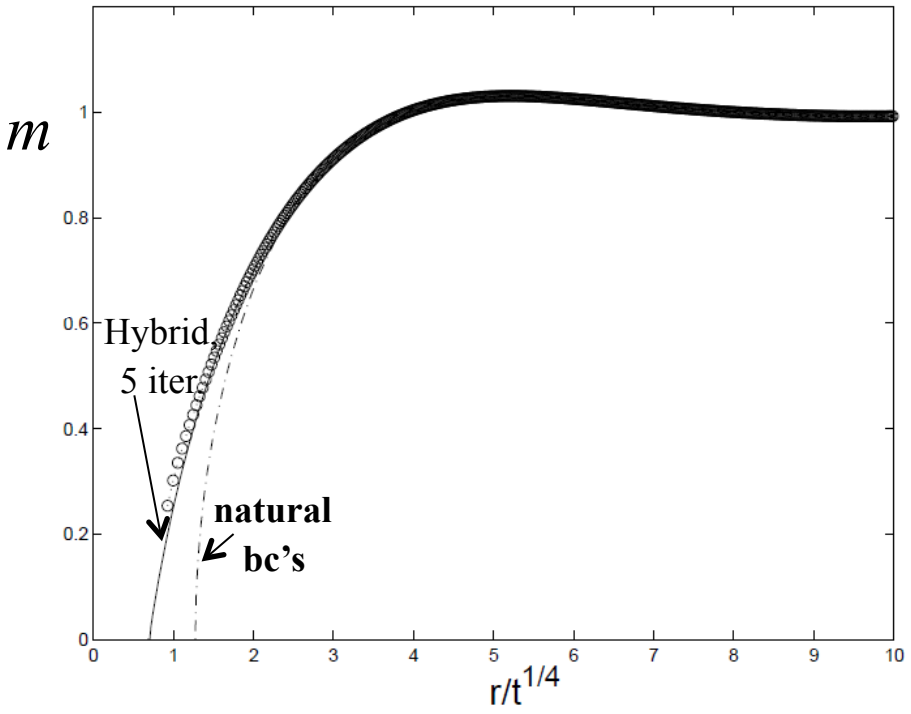
[Schneider, Nakamura, DM, 2014]

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.*]

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

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

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) ?

PDE in 1+1 dimensions; periodic profile

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

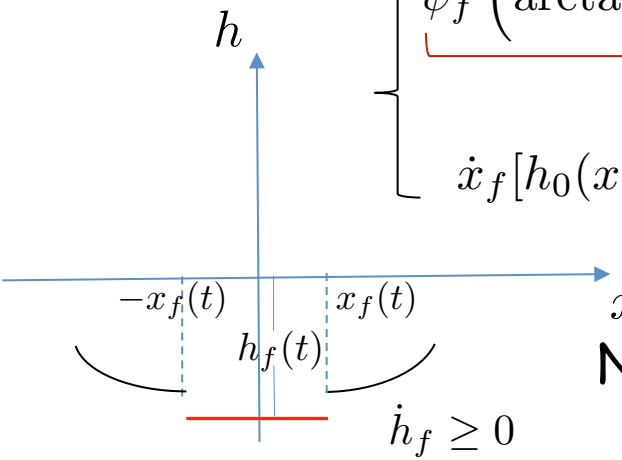
Neglect of $|h_x|h_x$ term

Goal: To **construct** a solution:
Formulate a system of ODEs for facet **height** and **position**.
Compare to **regularized** PDE

Claim: BC's at facet: $\begin{cases} \text{Facet speed by mass conservation} \\ \mu(x,t) = -\partial_x \tilde{\xi}(x,t) \text{ and } \tilde{\xi}(x,t) \text{: continuous in } x \end{cases}$

Bottom facet:

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



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

Numerical simulations of PDE and ODEs solutions

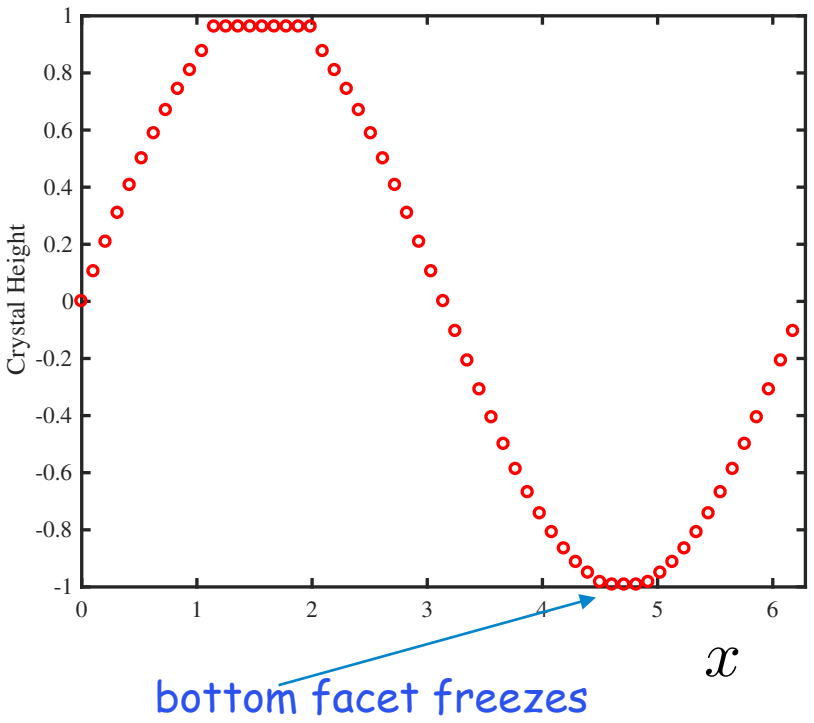
[Liu, Lu, DM, Marzuola, *subm.*]

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

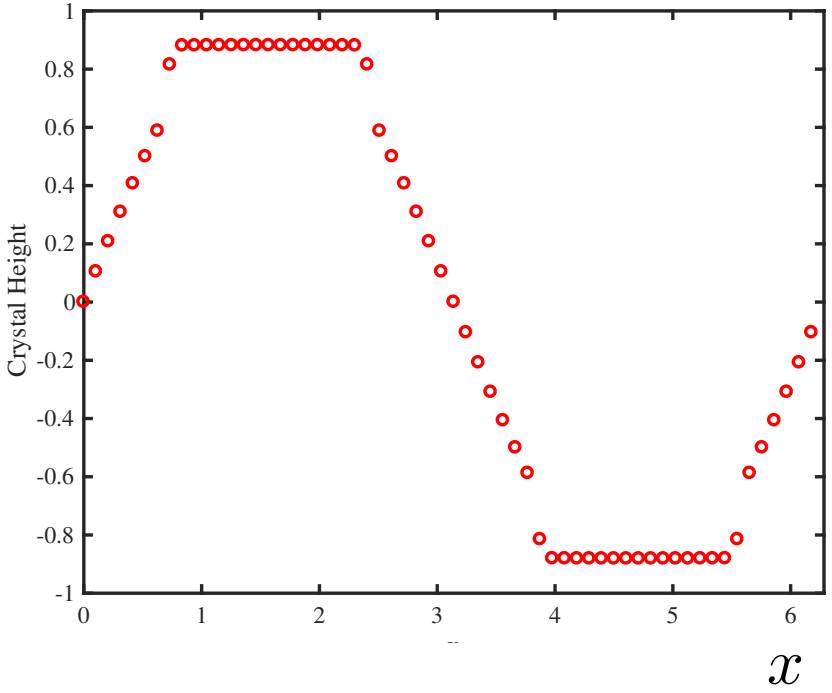
Exp. PDE (regularized):

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

h $\qquad$ $t = t_0 > 0$



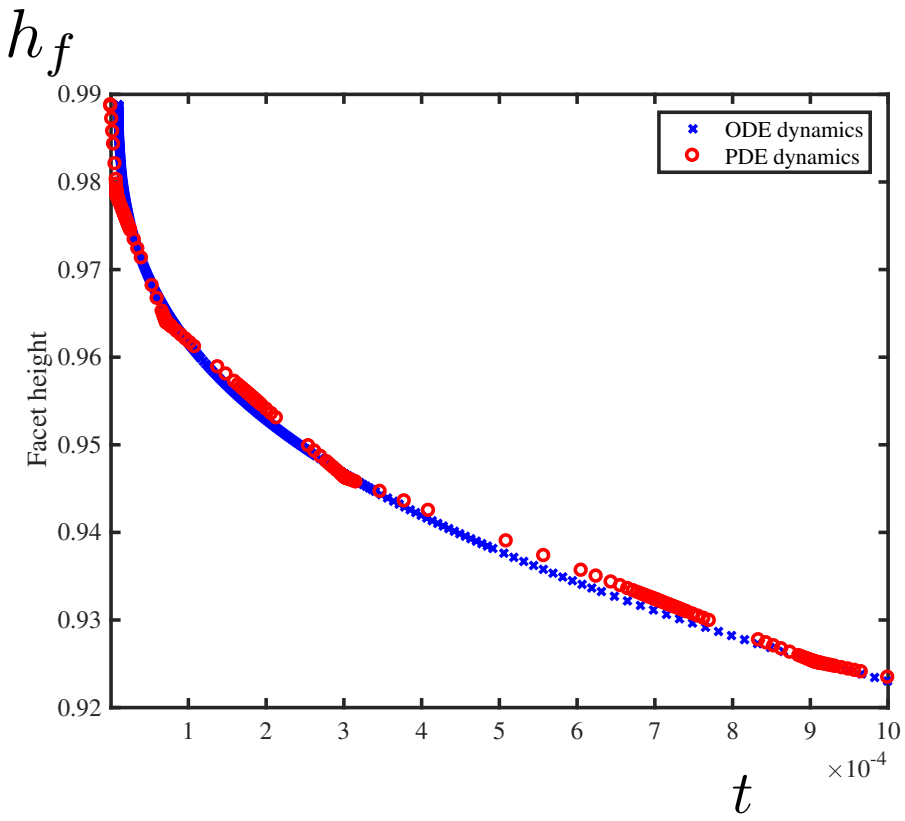
PDE by linearized exponential



Numerical simulations of PDE and ODE solutions (cont.)

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

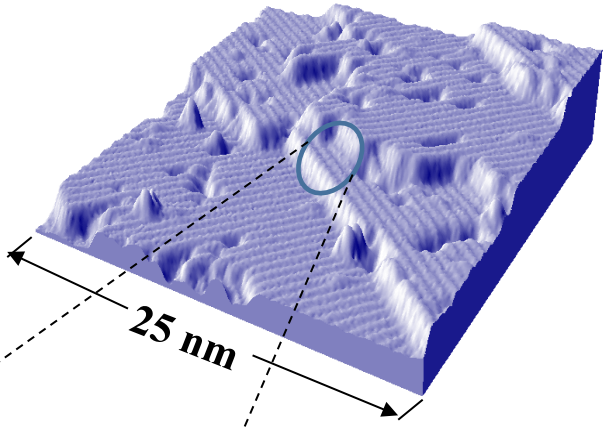
Facet height



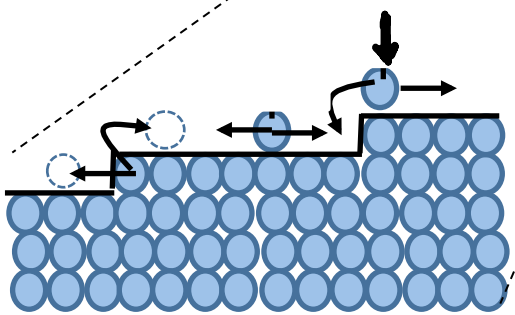
Open question: How does this prediction compare to step motion?

II. From atoms to step motion

Mesoscale



BCF (phenomenological) model:
Adatom diffusion/Fick's law +
Step velocity law +
Linear kinetic relation at step

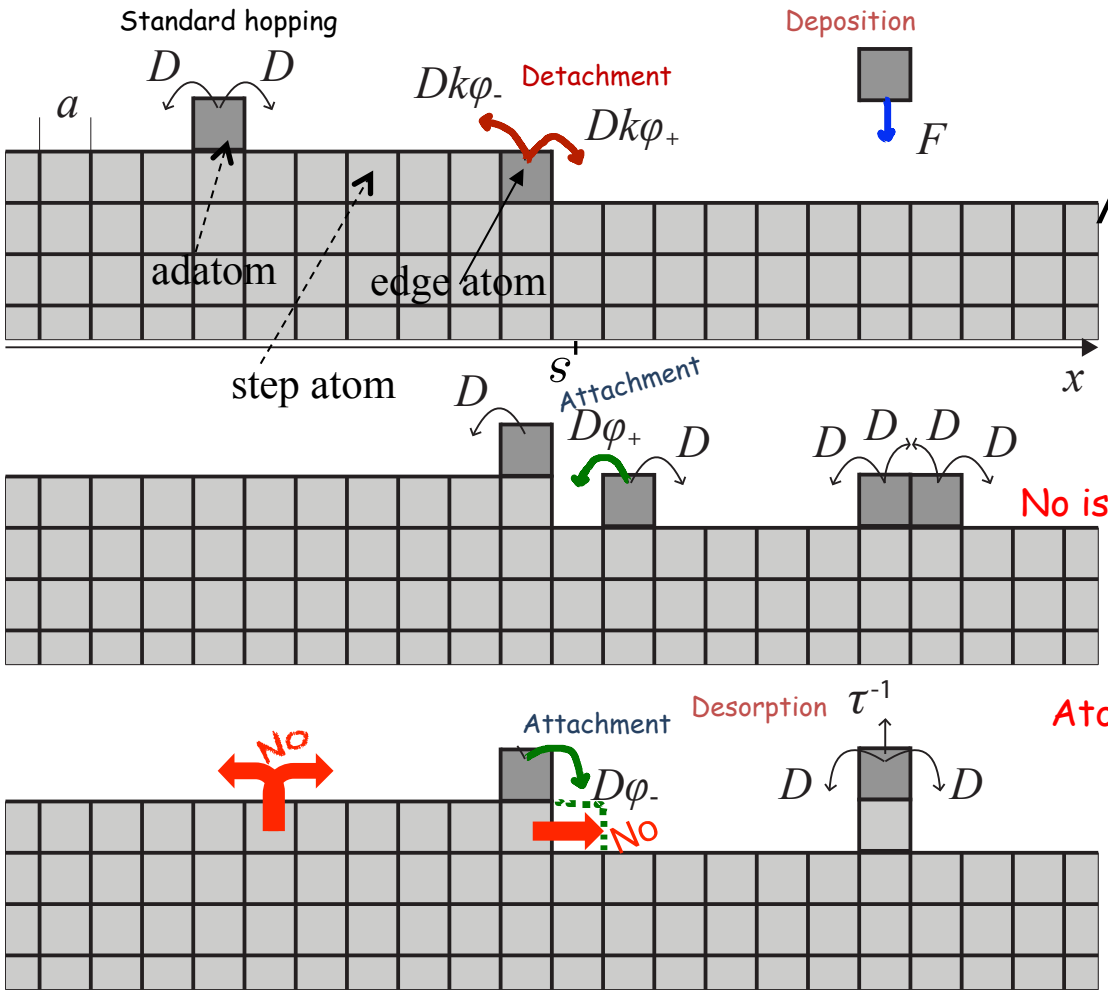


Kinetic restricted solid-on-solid model:
Atoms hop
in **1+1 dimensions**

[Patrone, DM, 2014; Patrone, Einstein, DM, 2014; Lu, Liu, DM, 2015; Schneider, DM, 2017; Schneider, Patrone, DM, 2018]

Atomistic scale: Basic transitions: Toy model

N lattice sites; $Na = \mathcal{O}(1)$ as $a \to 0$



Key parameters:

k and F/D

Position of edge atom can only change by -1, 0, 1 on lattice

Atomistic configurations and step motion

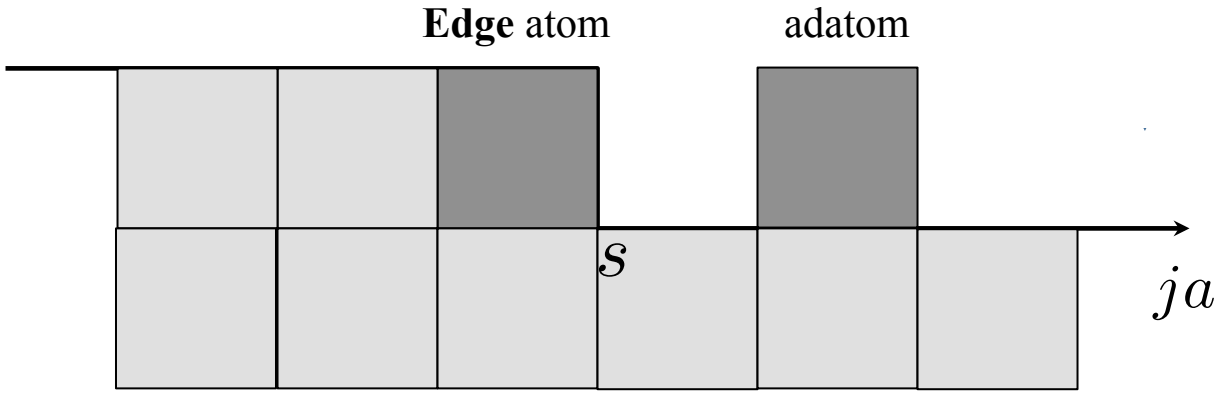
multiset: positions of adatoms

$(\boldsymbol{\alpha}, m)$: state of system

Mass of system (changed by deposition from above)

s_0: initial site for edge atom

m_0: initial mass



s: Microscale step position

$$s = \{s_0 - \underbrace{(|\boldsymbol{\alpha}| - |\boldsymbol{\alpha}_0|)}_{\text{adatom number increase}} \}a$$

Master equation

$$\dot{p}_{\boldsymbol{\alpha},m}(t) = \sum_{\boldsymbol{\alpha}',m'} T_{(\boldsymbol{\alpha},m),(\boldsymbol{\alpha}',m')} p_{\boldsymbol{\alpha}',m'}(t) \qquad \left(\sum_{\boldsymbol{\alpha},m} T_{(\boldsymbol{\alpha},m),(\boldsymbol{\alpha}',m')} = 0 \right)$$

$p_{\boldsymbol{\alpha}',m'}$: probability density for $(\boldsymbol{\alpha}', m')$

Average of Q: $\langle Q \rangle = \sum_{\boldsymbol{\alpha},m} Q(\boldsymbol{\alpha}, m) p_{\boldsymbol{\alpha},m}(t)$

Goal:
To obtain relations between
averages for step position and adatom density

[Schneider, DM, 2017; Schneider, Patrone, DM, 2018]

Marginal density

Definition. The *marginal probability density* is

$$p_{\boldsymbol{\alpha}}(t) = \sum_m p_{\boldsymbol{\alpha},m}(t)$$

The marginalized master equation is

$$\begin{aligned}\dot{p}_{\boldsymbol{\alpha}} &= \sum_{\boldsymbol{\alpha}'} \mathcal{T}_{\boldsymbol{\alpha},\boldsymbol{\alpha}'} p_{\boldsymbol{\alpha}'}(t) \\ &= D \sum_{\boldsymbol{\alpha}'} [A_{\boldsymbol{\alpha},\boldsymbol{\alpha}'} + \epsilon B_{\boldsymbol{\alpha},\boldsymbol{\alpha}'}] p_{\boldsymbol{\alpha}'}(t); \quad \epsilon = F/D \ .\end{aligned}$$

Diffusion, attachment/detach.

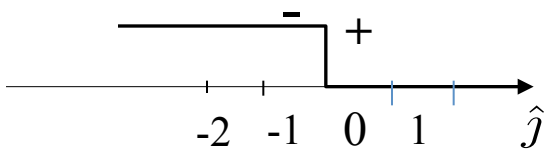
Deposition

PROPOSITION 1. *If a non-trivial steady-state solution, $p^{ss}_{\boldsymbol{\alpha}}$, of the marginalized master eq. exists, the solution $p_{\boldsymbol{\alpha}}(t)$ satisfies*

$$\max_{\boldsymbol{\alpha}} \frac{p_{\boldsymbol{\alpha}}(t)}{p^{ss}_{\boldsymbol{\alpha}}} \leq \max_{\boldsymbol{\alpha}} \frac{p_{\boldsymbol{\alpha}}(0)}{p^{ss}_{\boldsymbol{\alpha}}} \qquad (t > 0) \ .$$

Near equilibrium evolution: $\max_{\boldsymbol{\alpha}}\{p_{\boldsymbol{\alpha}}(0)/p^{ss}_{\boldsymbol{\alpha}}\} \leq C.$

Discrete averages: Definitions



Definition 1. The average step position is

$$\varsigma(t) = a \sum_{\boldsymbol{\alpha},m} \{s_0 - (|\boldsymbol{\alpha}| - |\boldsymbol{\alpha}_0|) + (m - m_0)\} p_{\boldsymbol{\alpha},m}(t) \ .$$

Definition 2. (i) The Eulerian adatom density is

$$\rho_j(t) = \sum_{\boldsymbol{\alpha},m} \nu_{j-s(\boldsymbol{\alpha},m)}(\boldsymbol{\alpha}) p_{\boldsymbol{\alpha},m}(t)/a \ .$$

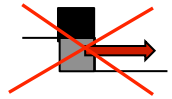
number of adatoms per site

(ii) The Lagrangian-type adatom density is defined by

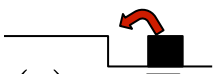
$$c_{\hat{j}} = \sum_{\boldsymbol{\alpha},m} \nu_{\hat{j}}(\boldsymbol{\alpha}) p_{\boldsymbol{\alpha},m}(t)/a = \sum_{\boldsymbol{\alpha}} \nu_{\hat{j}}(\boldsymbol{\alpha})\, p_{\boldsymbol{\alpha}}(t)/a \ .$$

Definition 3. Discrete adatom fluxes at step edge:

$$J_{\pm}(t) = \pm \sum_{\boldsymbol{\alpha},m} \mathbb{I}(\nu_{-1}(\boldsymbol{\alpha},m) = 0)$$

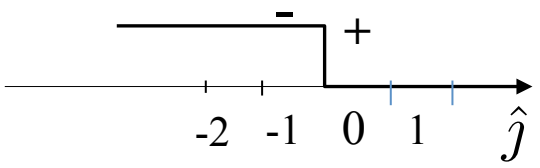


$$\times \left[T_{(\boldsymbol{\alpha}_{\pm},m),(\boldsymbol{\alpha},m)} p_{\boldsymbol{\alpha},m}(t) - T_{(\boldsymbol{\alpha},m),(\boldsymbol{\alpha}_{\pm},m)} p_{\boldsymbol{\alpha}_{\pm},m}(t) \right]$$



where $\boldsymbol{\alpha}_{\pm} = \widetilde{\boldsymbol{\alpha}} \cup \{\pm 1\}$ results by atom detachment $(\widetilde{\alpha} = \{i+1 \mid \forall i \in \alpha\})$

Discrete averages: Adatom density $(\tau \to \infty)$



Evolution of discrete adatom density (by **Def. 2** and master eq.):

$$\dot{\rho}_j(t) = D[\rho_{j-1}(t) - 2\rho_j(t) + \rho_{j+1}(t)] + \frac{F}{(N-1)a}$$ discrete diffusion

$$- D[R_{j-1}(t) - 2R_j(t) + R_{j+1}(t)]$$ high-occupation correction

$+$ boundary (step-edge) terms

$$R_j(t) = \sum_{\boldsymbol{\alpha},m} \left[\nu_{j-s(\boldsymbol{\alpha},m)}(\boldsymbol{\alpha}) - \mathbb{1}(\nu_{j-s(\boldsymbol{\alpha},m)}(\boldsymbol{\alpha}) > 0)\right] p_{\boldsymbol{\alpha},m}(t)/a$$

by 2-particle
or highly occupied states

Discrete averages: Kinetic relation at step edge

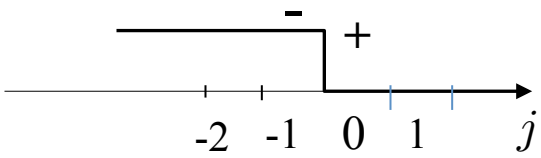
Mass Flux (Def.3)

Linear kinetic term correction

$$J_{\pm}(t) = \mp D\phi_{\pm} a\,[c_{\pm 1}(t) - c^{eq}] \mp D\phi_{\pm} a f_{\pm}(t)$$

From F=0: equil. soln. of master eqn.

$$c^{eq} = \frac{\langle n \rangle}{(N-1)a} = \frac{k/a}{1-k}$$



$$f_{+}(t) = k\left[c^{eq} + \sum_{\boldsymbol{\alpha}} \mathbb{1}(\nu_{-1}(\boldsymbol{\alpha}) > 0) p_{\boldsymbol{\alpha}}(t)/a\right] - \sum_{\boldsymbol{\alpha}} \mathbb{1}(\nu_1(\boldsymbol{\alpha}) > 1)\nu_1(\boldsymbol{\alpha}) p_{\boldsymbol{\alpha}}(t)/a$$

$$f_{-}(t) = k\left[c^{eq} + \sum_{\boldsymbol{\alpha}} \mathbb{1}(\nu_{-1}(\boldsymbol{\alpha}) > 0) p_{\boldsymbol{\alpha}}(t)/a\right] - \sum_{\boldsymbol{\alpha}} \mathbb{1}(\nu_1(\boldsymbol{\alpha}) > 0)\nu_{-1}(\boldsymbol{\alpha}) p_{\boldsymbol{\alpha}}(t)/a - \sum_{\boldsymbol{\alpha}} \mathbb{1}(\nu_1(\boldsymbol{\alpha}) = 0)\mathbb{1}(\nu_{-1}(\boldsymbol{\alpha}) > 1) \times [\nu_{-1}(\boldsymbol{\alpha}) - 1]\, p_{\boldsymbol{\alpha}}(t)/a\ .$$

Accumulation of adatoms

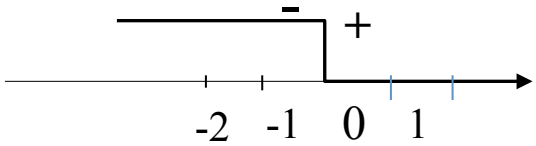
BCF model, corrections, and estimates

[Schneider, Patrone, DM, 2018]

Linear kinetic relation $D\phi_\pm a = O(1)$

$$J_\pm(t) = \mp D\phi_\pm a\,[c_{\pm 1}(t) - c^{eq}] \mp D\phi_\pm a f_\pm(t)$$

correction



correction

Also: $$J_\pm(t) = \mp Da\,[c_{\pm 2}(t) - c_{\pm 1}(t)] \mp Da\left[\hat{R}_{\pm 2}(t) - \hat{R}_{\pm 1}(t)\right]$$

PROPOSITION 2. *For near-equilibrium evolution,* $f_\pm(t)$ *obey*

$$f_\pm(t) \le \mathcal{C}_1 \frac{k}{1-k}\frac{k}{a} + \mathcal{C}_2 \frac{\epsilon N}{(1+\phi_\pm)a} \ .$$

In the same vein, the corrections $\hat{R}_j(t)$ *satisfy*

$$\hat{R}_j(t) \le \mathcal{C}_1 \frac{k}{1-k}\frac{k}{a} + \mathcal{C}_2 \frac{\epsilon N}{a} \qquad (\epsilon = F/D) \ .$$

Dilute regime: $k \le \mathcal{O}(a)$ and $\epsilon N \ll \mathcal{O}(a)$; corrections are negligible

➡ BCF model emerges

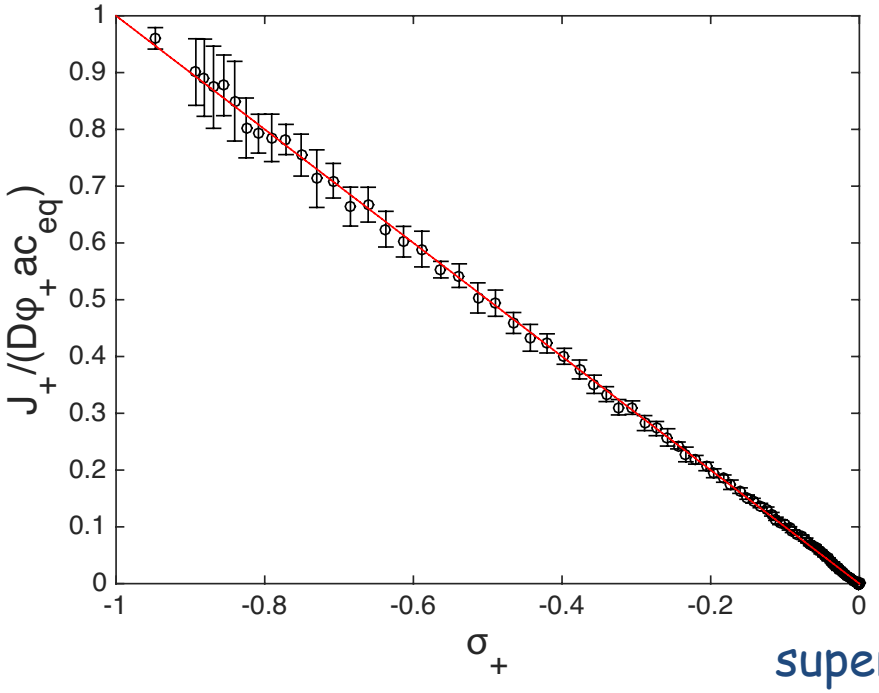
Kinetic Monte Carlo (KMC) simulations: Flux

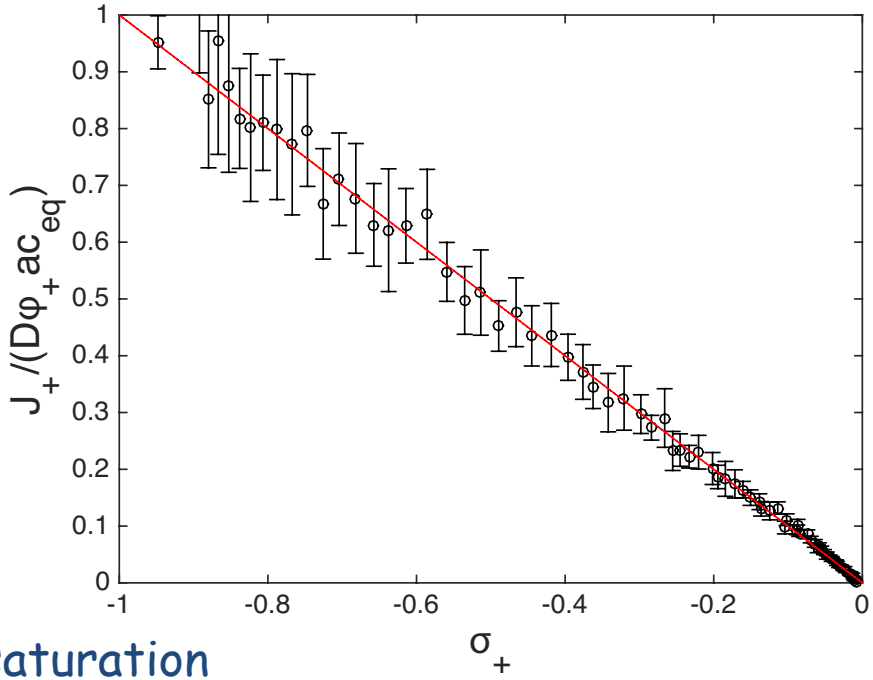
Dilute regime

$F = 0,\ k = 2.5 \times 10^{-3}$

$\epsilon = F/D = 10^{-3}$

$k = 2.5 \times 10^{-3}$





supersaturation

$\sigma_+ := (c_1 - c^{eq})/c^{eq}$

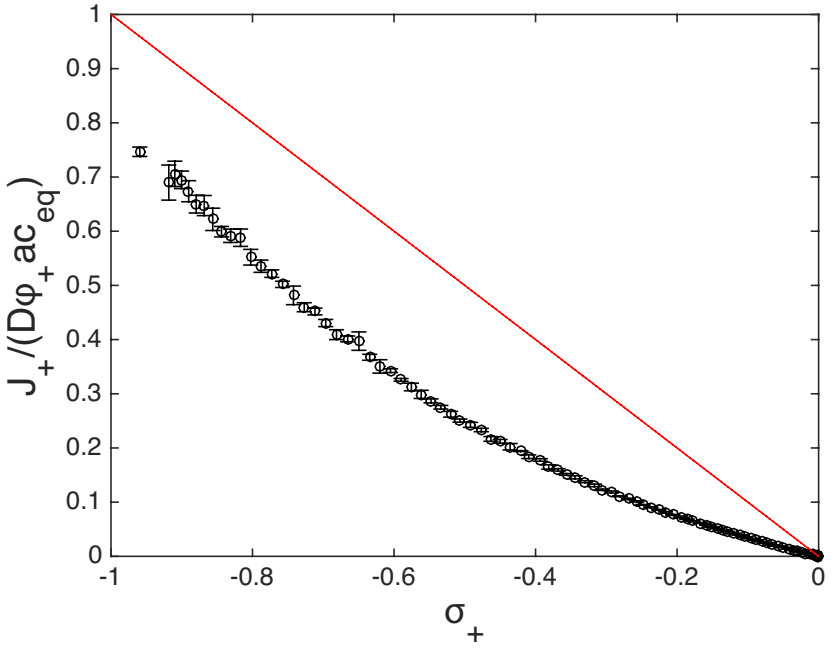
KMC simulations: Flux (cont.)

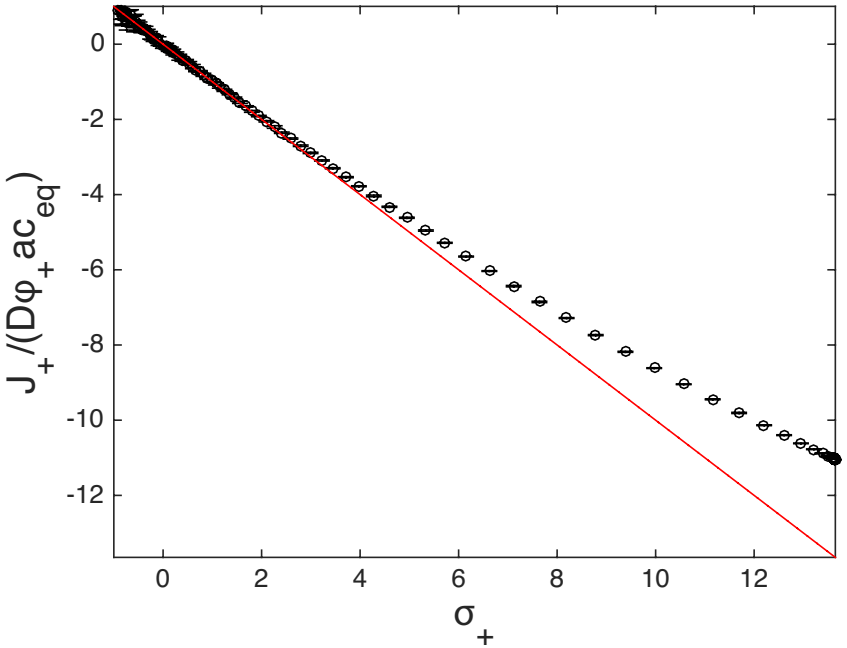
Non-dilute regime

$$\epsilon = F/D = 4 \times 10^{-2}$$

$$F = 0,\ k = 0.2$$

$$k = 2.5 \times 10^{-3}$$





supersaturation

$$\sigma_+ := (c_1 - c^{eq})/c^{eq}$$

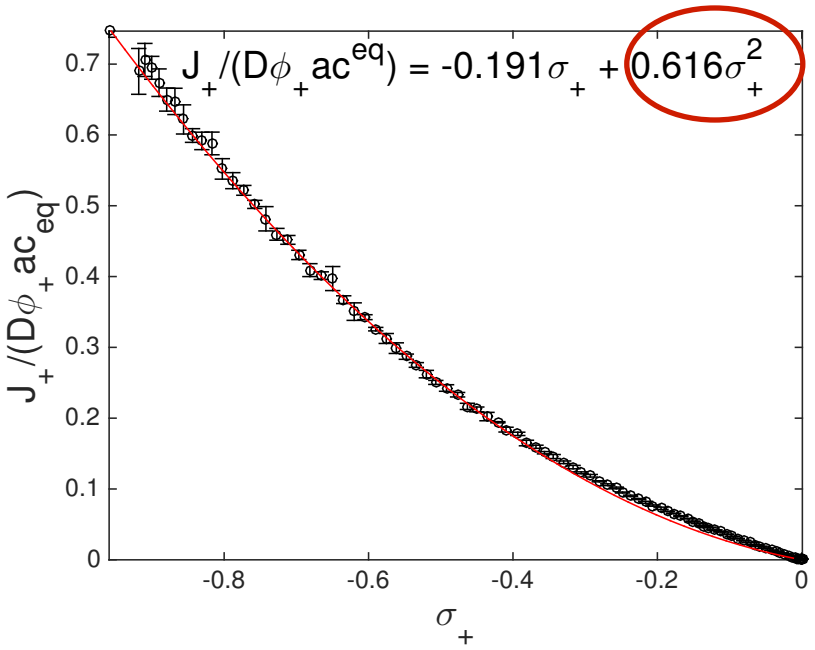
Corrections to BCF model: Fitting to KMC data

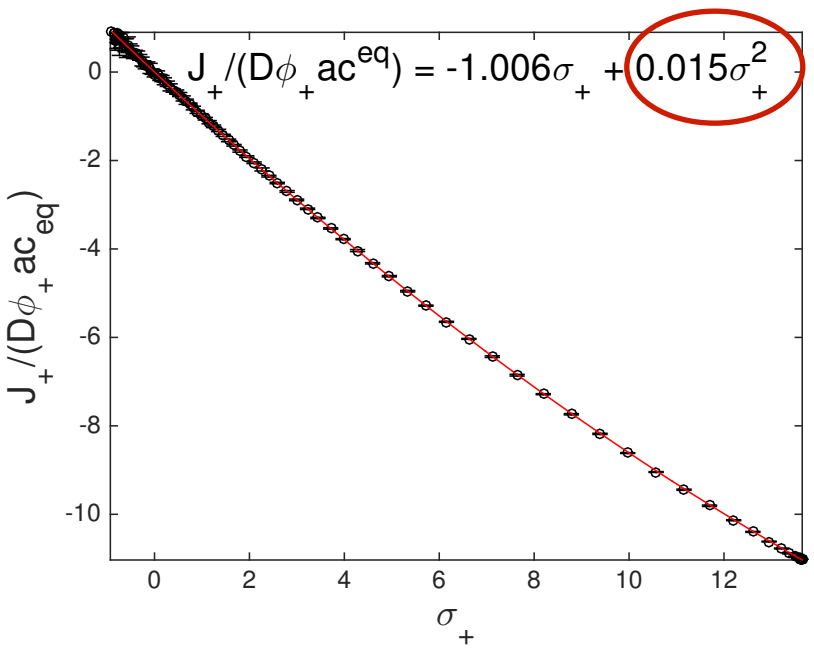
Non-dilute regime

$$\epsilon = F/D = 4 \times 10^{-2}$$

$$F = 0,\ k = 0.2$$

$$k = 2.5 \times 10^{-3}$$





Can one derive explicit formulas for the coefficients?
Extensions to higher dimension (curved steps) ?

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

- 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?

- By master eq. for adatoms in 1+1 dims, BCF description arises in low-supersaturation regime of atomistic model.

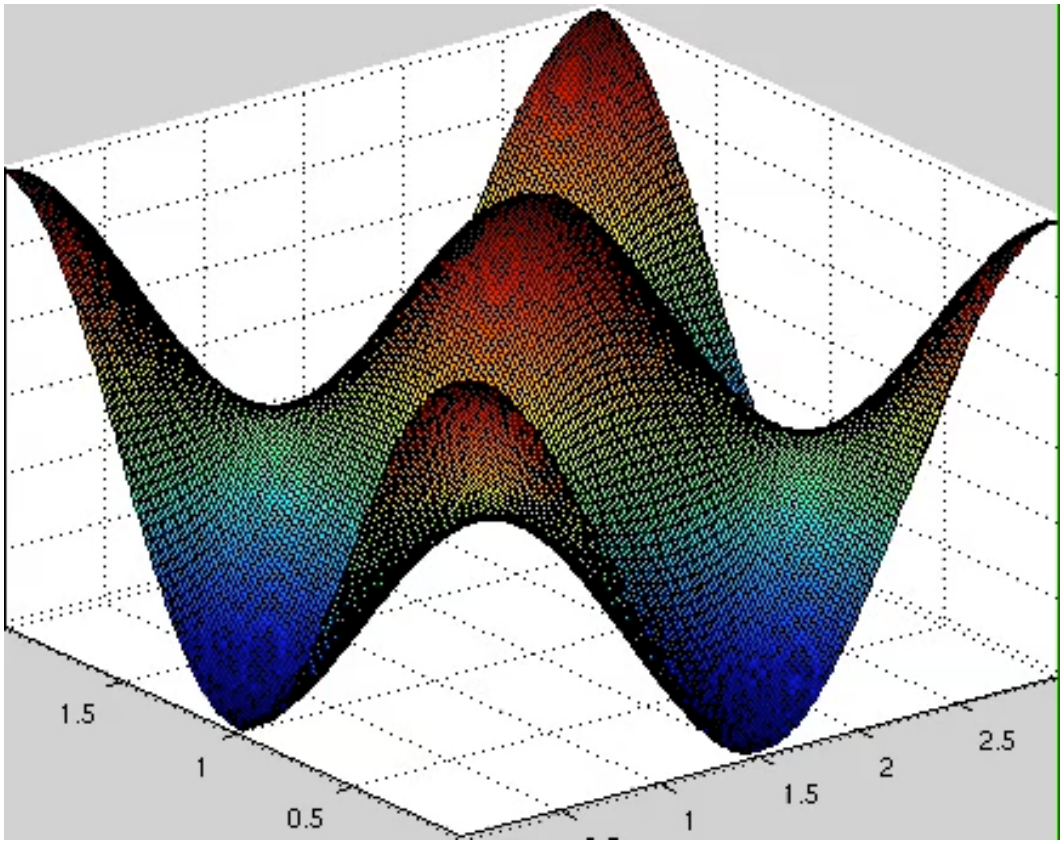
- For high enough supersaturation, linear kinetic relation for adatom flux has nonlinear corrections, estimated in toy model.
  Emergence of step model from atomistic dynamics in 2+1 dimensions?

Numerical simulations: Bi-periodic profiles, $g_1=0$ (no facets form)

Tensor **M**

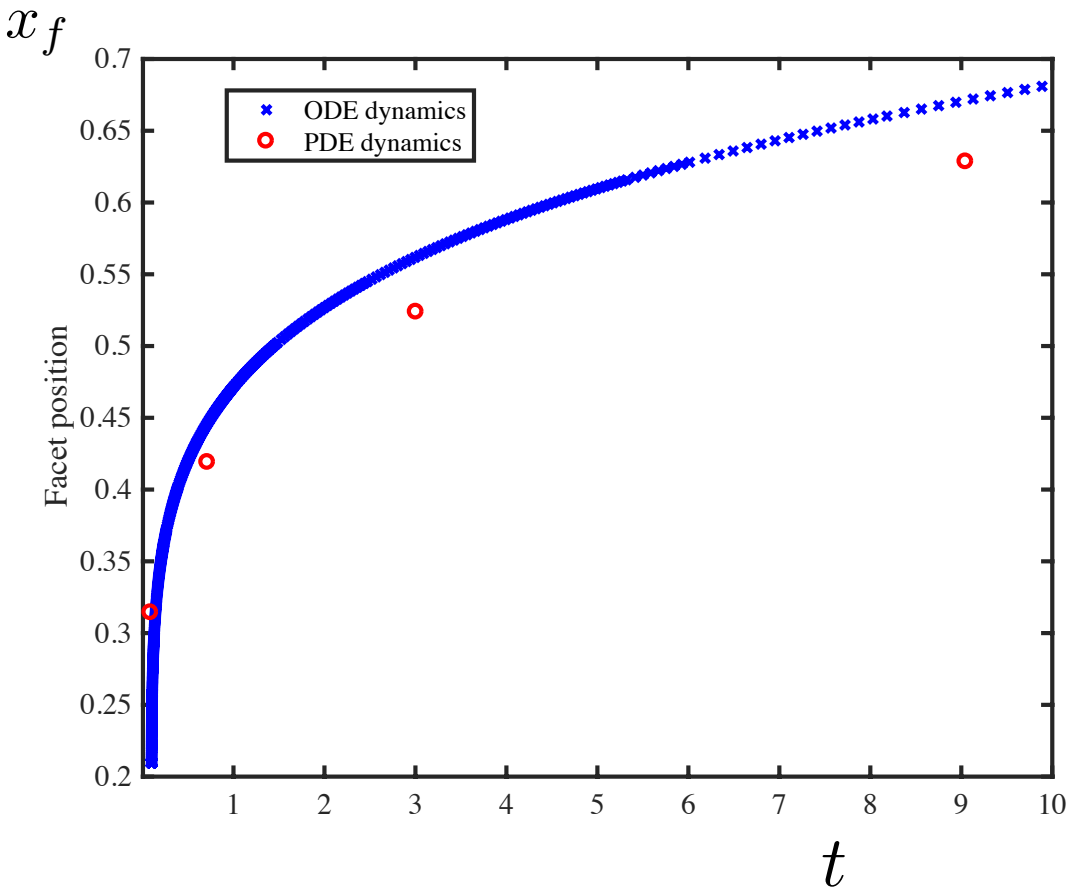
[Bonito, Nochetto, Quah, DM, 2009]

h



Transition to 1D profile!

Numerical simulations of PDE vs ODEs (cont.)



Equilibrium prob. density in closed form

- $\tau \to \infty$, $F\tau \to 0$: (Mass conserving)

$$p^{ss}_{\boldsymbol{\alpha},m} = p^{eq}_{\boldsymbol{\alpha}} = (1-k)^{N-1} k^{|\boldsymbol{\alpha}|}$$

- $1 < F\tau < (N-1)k$:

$$p^{eq}_{\boldsymbol{\alpha},m} = (1-k)^{N-1} k^{|\boldsymbol{\alpha}|} (1-\mathcal{R}) \mathcal{R}^{m-m_0}$$

$$\mathcal{R} = \frac{F\tau}{(N-1)k}$$

Property of marginalized master equation

PROPOSITION 1. *If a non-trivial steady-state solution, $p^{ss}_{\boldsymbol{\alpha}}$, of the marginalized master equation exists, then any solution $p_{\boldsymbol{\alpha}}(t)$ satisfies*

$$\max_{\boldsymbol{\alpha}} \frac{p_{\boldsymbol{\alpha}}(t)}{p^{ss}_{\boldsymbol{\alpha}}} \leq \max_{\boldsymbol{\alpha}} \frac{p_{\boldsymbol{\alpha}}(0)}{p^{ss}_{\boldsymbol{\alpha}}} \ , \quad t > 0 \ .$$

Proof. We have

$$\begin{aligned} \dot{p}_{\boldsymbol{\alpha}}(t) &= \mathcal{T}_{\boldsymbol{\alpha},\boldsymbol{\alpha}} p_{\boldsymbol{\alpha}}(t) + \sum_{\boldsymbol{\alpha}' \neq \boldsymbol{\alpha}} \mathcal{T}_{\boldsymbol{\alpha},\boldsymbol{\alpha}'} p_{\boldsymbol{\alpha}'}(t) \\ &= \mathcal{T}_{\boldsymbol{\alpha},\boldsymbol{\alpha}} p^{ss}_{\boldsymbol{\alpha}} \frac{p_{\boldsymbol{\alpha}}(t)}{p^{ss}_{\boldsymbol{\alpha}}} + \sum_{\boldsymbol{\alpha}' \neq \boldsymbol{\alpha}} \mathcal{T}_{\boldsymbol{\alpha},\boldsymbol{\alpha}'} p^{ss}_{\boldsymbol{\alpha}'} \frac{p_{\boldsymbol{\alpha}'}(t)}{p^{ss}_{\boldsymbol{\alpha}'}} \\ \left(\sum_{\boldsymbol{\alpha}'} \mathcal{T}_{\boldsymbol{\alpha},\boldsymbol{\alpha}'} p^{\mathrm{ss}}_{\boldsymbol{\alpha}'} = 0 \right) \qquad &= \sum_{\boldsymbol{\alpha}' \neq \boldsymbol{\alpha}} \mathcal{T}_{\boldsymbol{\alpha},\boldsymbol{\alpha}'} p^{ss}_{\boldsymbol{\alpha}'} \left\{ \frac{p_{\boldsymbol{\alpha}'}(t)}{p^{ss}_{\boldsymbol{\alpha}'}} - \frac{p_{\boldsymbol{\alpha}}(t)}{p^{ss}_{\boldsymbol{\alpha}}} \right\} \ . \end{aligned}$$

Note that $\mathcal{T}_{\boldsymbol{\alpha},\boldsymbol{\alpha}'} p^{ss}_{\boldsymbol{\alpha}'} \geq 0$ for all $\boldsymbol{\alpha}' \neq \boldsymbol{\alpha}$. If $\boldsymbol{\alpha}$ maximizes (minimizes) $p_{\boldsymbol{\alpha}'}(t)/p^{ss}_{\boldsymbol{\alpha}'}$ over all $\boldsymbol{\alpha}'$, then $\dot{p}_{\boldsymbol{\alpha}}(t) \leq 0$ ($\dot{p}_{\boldsymbol{\alpha}}(t) \geq 0$). □

Near equilibrium evolution: $\max_{\boldsymbol{\alpha}} \{ p_{\boldsymbol{\alpha}}(0)/p^{ss}_{\boldsymbol{\alpha}} \} \leq C$.