(Lecture III)
From discrete schemes to macroscopic evolution laws: II. Crystal facets & boundary conditions

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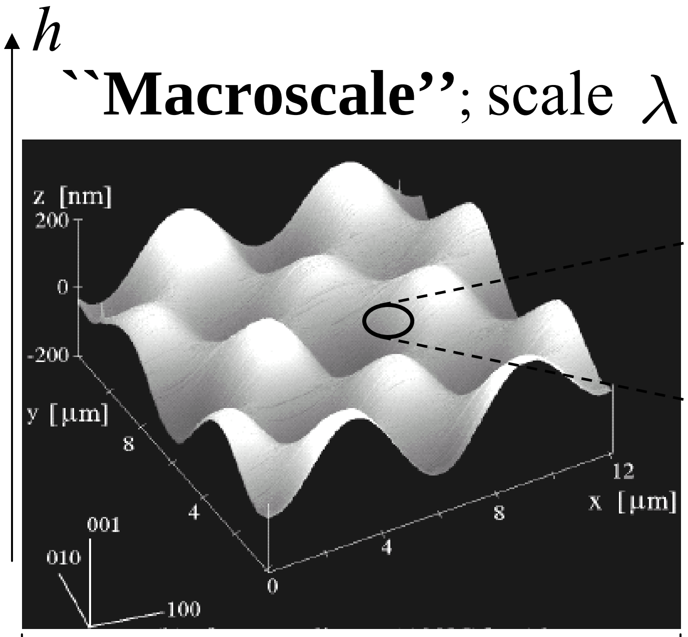
Research supported by ***NSF*** *DMS-0847587*

Interdisciplinary Conference "**Mathematical Aspects of Crystal Growth**"
Hokkaido University
Sapporo, Japan -- July 26-30, 2010

Physical setting: Two Scales

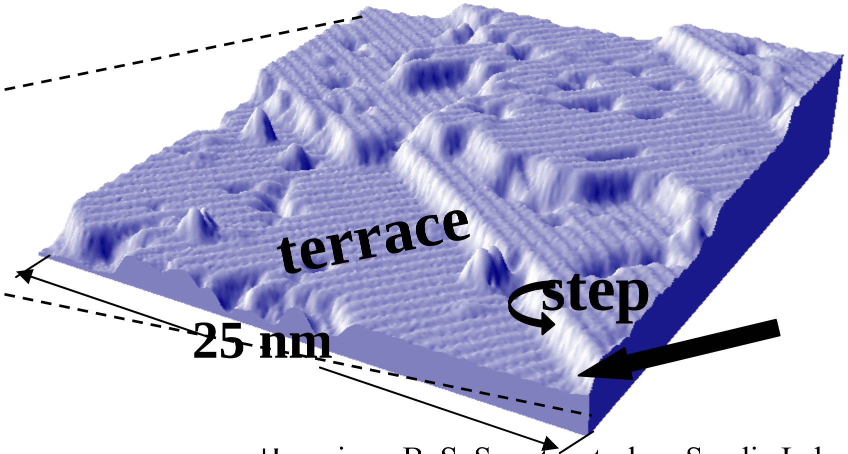
``**Macroscale**''; scale λ



20 μm

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

Nanoscale [same material/orientation]



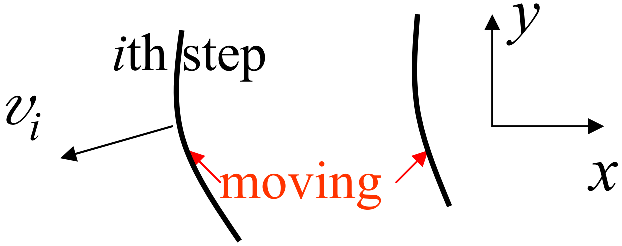
~1 atom;

height a

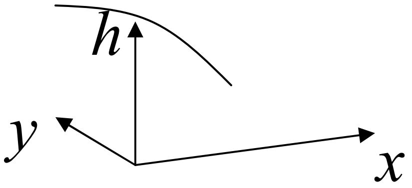
[Imaging : B. S. Swartzentruber, Sandia Lab, 2002]

Motion of ***steps***:

Discrete scheme



PDE for height h



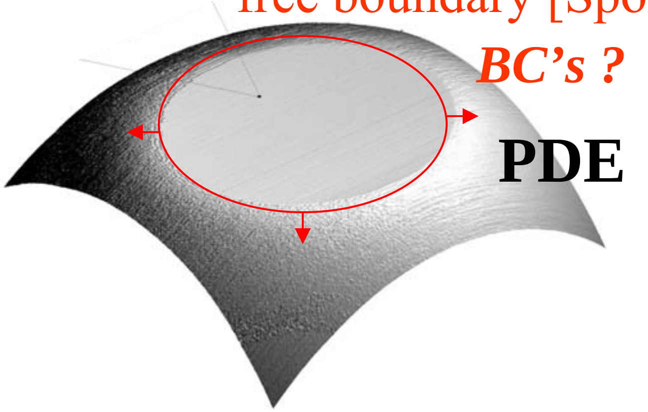
Notion of facet

Crystals have ***macroscopically flat surface regions***: **facets**

Macroscopic view:

free boundary [Spohn, 1993];

BC's ?



PDE

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

Complication:

Microscale motion on top

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

How do Boundary Conditions and local behavior
for continuum-scale slope
emerge from moving steps?

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

Review: Relaxation PDE outside facets

[DM, Kohn, 2006]

$$E[h] = \int \tilde{\gamma}\; dx \qquad \tilde{\gamma} = g_0 + g_1|\nabla h| + \frac{1}{3}g_3|\nabla h|^3$$

- $\frac{\mathrm{d}E_N^{st}}{\mathrm{d}t} = \sum_i \int_{L_i} \mathrm{d}s\; \upsilon_i \mu_i$:

step veloc.

$$\mu_i \Rightarrow \mu = \left(\frac{\delta E}{\delta h}\right)_{L^2} = -\mathrm{div}\left[\frac{\partial \tilde{\gamma}}{\partial \nabla h}\right]$$

Step chemical potential

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

Terrace flux

$J_{i,\perp} \propto \rho_i - \rho_0(1 + \beta\mu_i)$

$$\Rightarrow \boldsymbol{J} \propto -\boldsymbol{M}(\nabla h)\cdot\nabla\mu$$

Tensor mobility

Flux (Fick's law)

- $\upsilon_i = J_{i-1,\perp} - J_{i,\perp}$

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

mass conservation

4th-order, parabolic PDE for *h*

Diffusion Limited Case

$$\boldsymbol{M} = \text{const} \;:\; \frac{\partial h}{\partial t} \propto \Delta\frac{\delta E}{\delta h}$$

H^{-1} steepest descent for *E*

Steepest descent structure: formalities

$$E[h(\cdot,t)] = \int \tilde{\gamma}(\nabla h(x,t)) \ \mathrm{d}x$$

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \int \frac{\partial\tilde{\gamma}}{\partial\nabla h} \cdot \nabla h_t = \left\langle -\operatorname{div}\left[\frac{\partial\tilde{\gamma}}{\partial\nabla h}\right], h_t \right\rangle_{L^2} = \left\langle \Delta\operatorname{div}\left[\frac{\partial\tilde{\gamma}}{\partial\nabla h}\right], h_t \right\rangle_{H^{-1}}$$

Fastest decay:

$$\Rightarrow h_t = -\Delta\operatorname{div}\left[\frac{\partial\tilde{\gamma}}{\partial\nabla h}\right] = -\left(\frac{\delta E}{\delta h}\right)_{H^{-1}}$$

Recall: $\langle f, g \rangle_{H^{-1}} = \langle -\Delta^{-1} f, g \rangle_{L^2}$

Evolution occurs by most rapid energy decay, in certain sense

With facet, PDE is re-formulated respecting steepest descent

Facets are special

Difficulty: $\dfrac{\delta E}{\delta h}$ is **not** defined locally (usual sense) on facets

Possible remedies:

- By **fully continuum theory**: Treat facet as weak solution; apply *subgradient formulation* (PDE technique). This entails **certain** "natural boundary conditions"

  "thermodynamic approach"

2nd-order systems: Kobayashi, Giga, 1999; Giga, Giga, Kobayashi, 1999…
4th-order systems: Kashima, 2004; Odisharia, 2006;
DM, Aziz, Stone, 2005; Spohn 1993; Hager, Spohn, 1995; Shenoy, Freund, 2002;
Bonzel, Preuss, Steffen, 1984

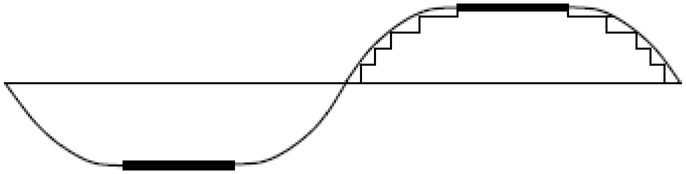
- By **(discrete) step motion** near facet [e.g., Israeli, Kandel, 1999]

How are the two approaches related ?

Past theoretical studies: Two main (relatively tractable) geometries

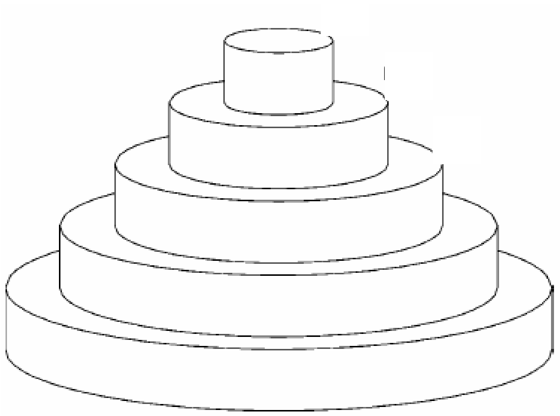
1D periodic profile

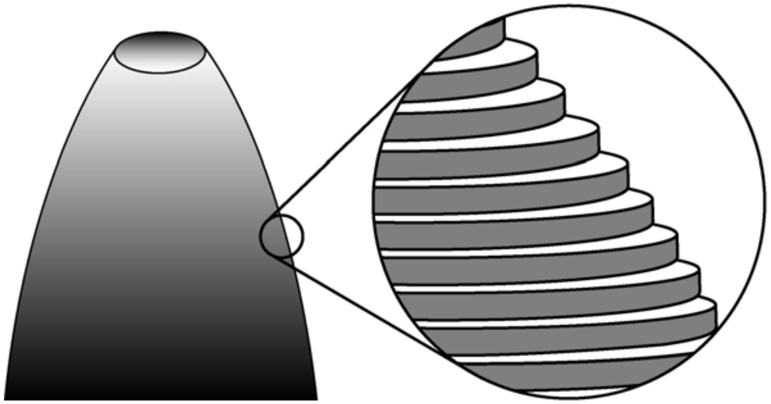
Some controversy
on how **extremal steps** interact



[Villain, 1986; Rettori, Villain, 1988; Ozdemir,Zangwill, 1990; Hager, Spohn, 1995; Bonzel, Mullins, 1996; Israeli, Kandel, 2000; Shenoy, Freund, 2002; **Odisharia (PhD Th), 2006**]

2D axisymmetric profile (cone)

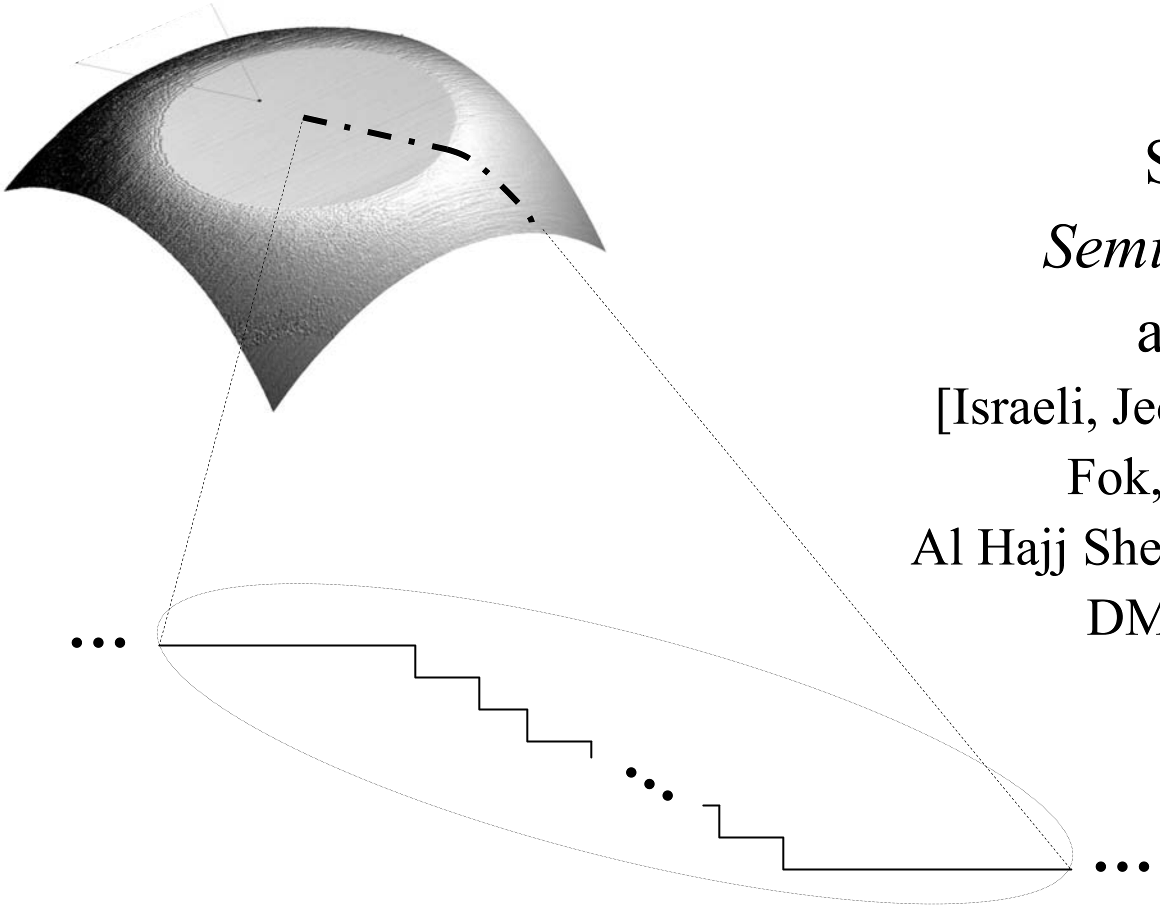




Uwaha, 1987; Tanaka *et al*., 1997; Krug, 1997;Israeli, Kandel, 98, 99, 02; Uwaha, Watanabe, 2000; Ichimiya *et al*., 2000; Thuermer *et al*., 2001; DM, Aziz, Stone, 2006; Fok, Rosales, DM, 2008]

Are there step schemes consistent with PDE solution near facets ?

Model: Finite-height step train



Simplification:

Semi-infinite **1D** facets

at **fixed** heights

[Israeli, Jeong, Kandel, Weeks, 2000;

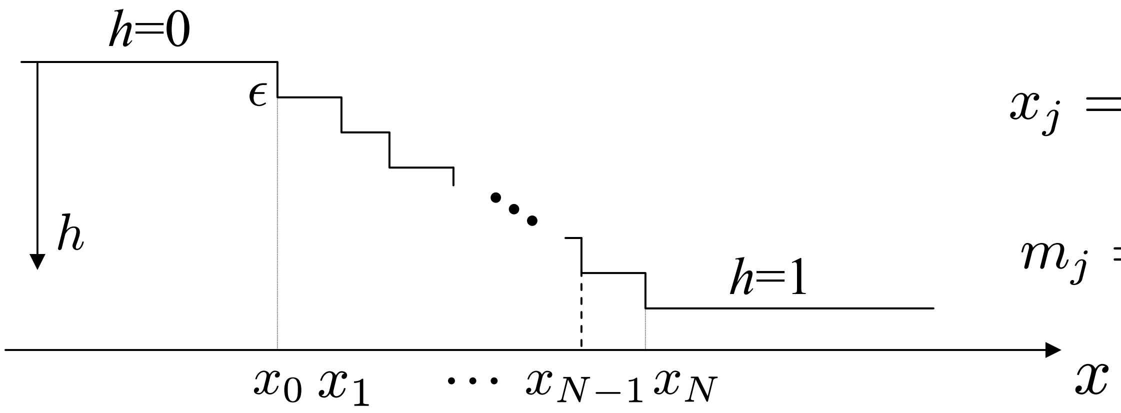
Fok, Rosales, DM, 2008;

Al Hajj Shehadeh, Kohn, Weare, *prepr*;

DM, Nakamura, *prepr*]

Diffusion-Limited (DL) kinetics: Numerical simulation

[Fok, Rosales, DM, 2008]



$$x_j = x_j(t)$$

$$m_j = \frac{\epsilon}{x_{j+1} - x_j};\ j = 0, \ldots, N-1$$

Discrete slopes

terrace diffusivity

Discrete scheme -- ***Diffusion Limited*** (DL) kinetics: $D_s m_j \ll k\epsilon$

attach.-detach. rate

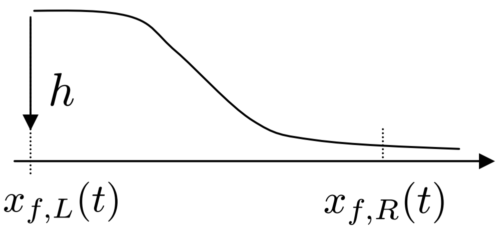
$$\dot{x}_j = \epsilon^{-3}[m_j(m_{j+1}^3 - 2m_j^3 + m_{j-1}^3) - m_{j-1}(m_j^3 - 2m_{j-1}^3 + m_{j-2}^3)]; \quad j{=}2,3,\ldots,N{-}3$$

Extremal steps

$$\begin{aligned} \dot{x}_0 &= \epsilon^{-3} m_0 (m_1^3 - 2m_0^3) \\ \dot{x}_1 &= \epsilon^{-3}[m_1(m_2^3 - 2m_1^3 + m_0^3) - m_0(m_1^3 - 2m_0^3)] \\ \dot{x}_{N-1} &= \epsilon^{-3}[m_{N-1}(m_{N-2}^3 - 2m_{N-1}^3) - m_{N-2}(m_{N-1}^3 - 2m_{N-2}^3 + m_{N-3}^3)] \\ \dot{x}_N &= -\epsilon^{-3} m_{N-1}(m_{N-2}^3 - 2m_{N-1}^3) \end{aligned}$$

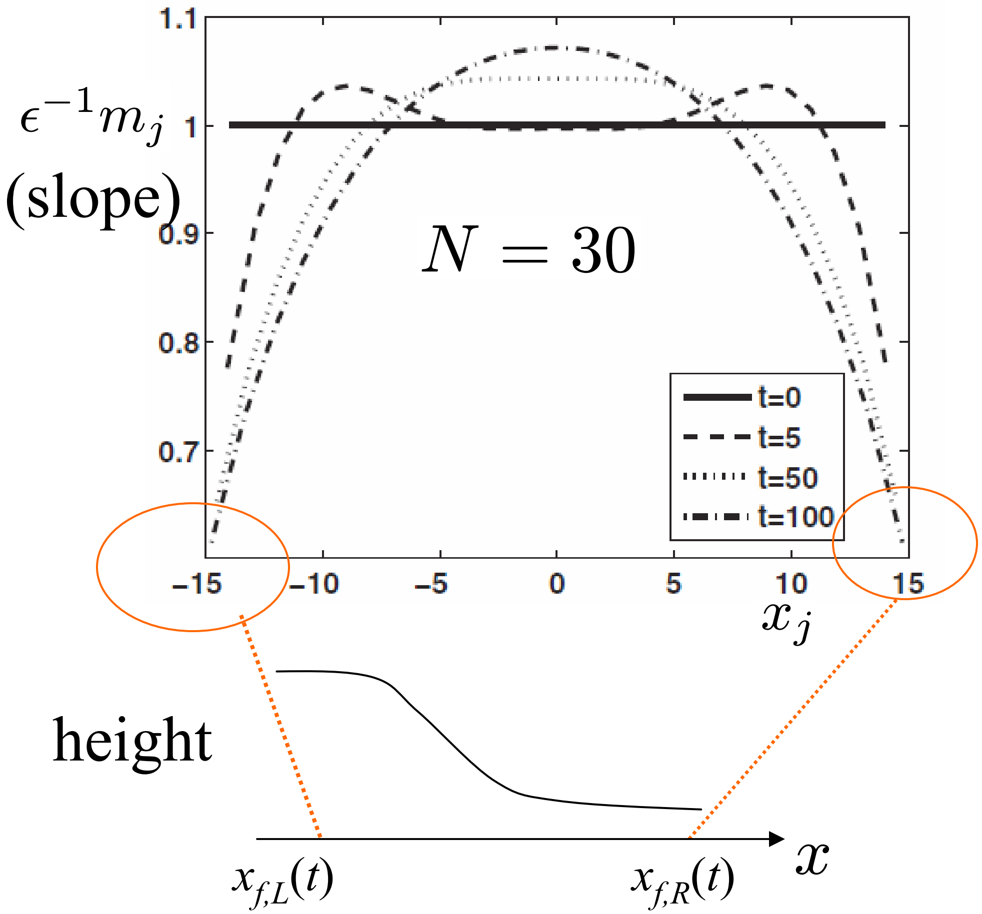
PDE for continuum slope *m* away from facet edges:

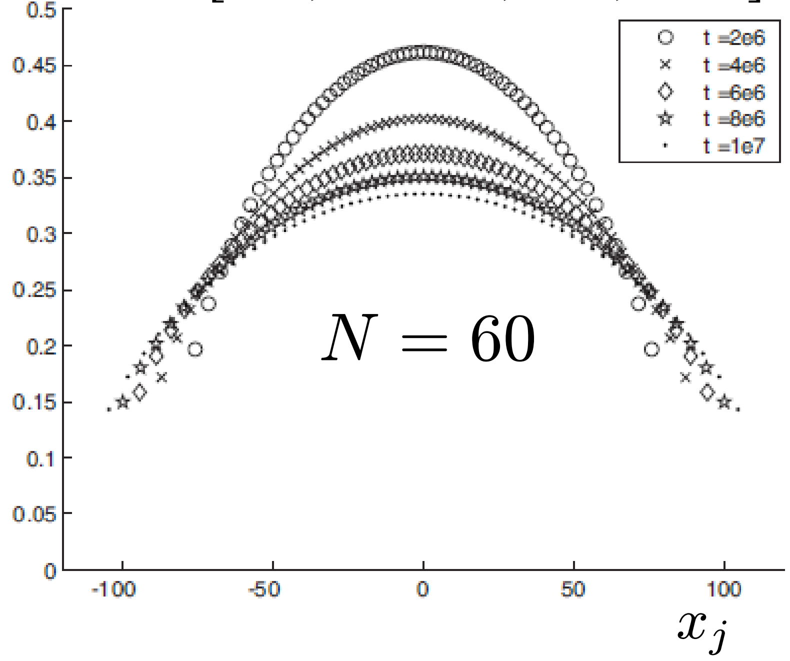
$$\partial_t m = -\partial_x^4(m^2) \quad x_{f,L}(t) < x < x_{f,R}(t);\ m = |h_x|$$



DL kinetics: Numerical simulation (cont.)

[Fok, Rosales, DM, 2008]





Observation: At long enough times, slope settles to self-similar form

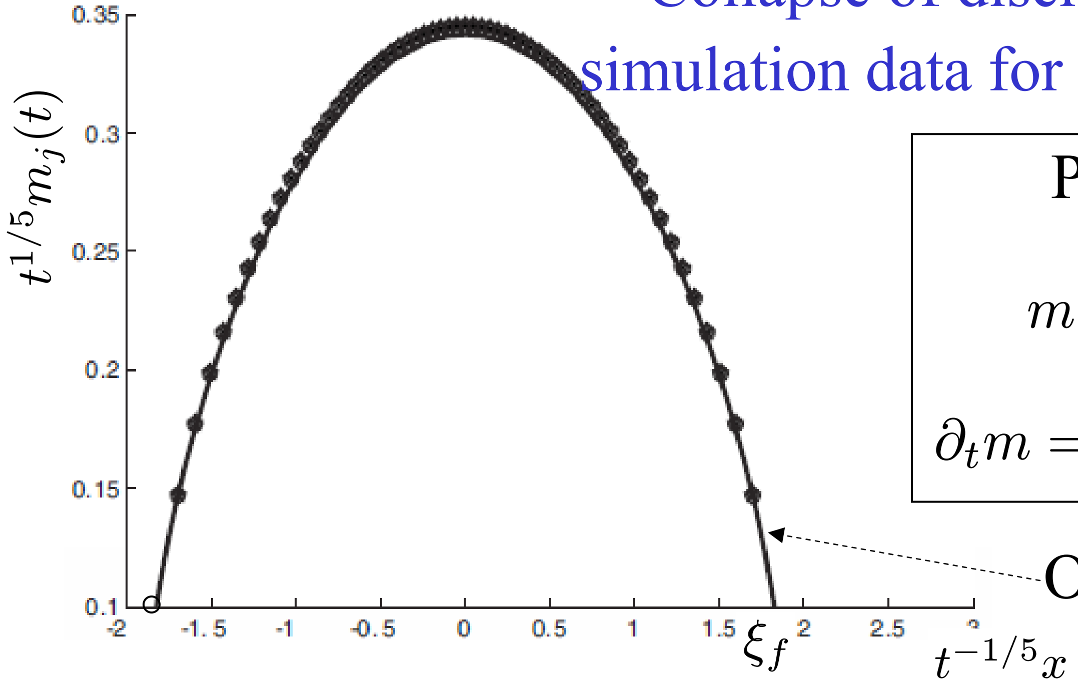
$$m_j(t) \sim t^{-1/5} M(x_j t^{-1/5})$$

Consistent with
ODEs and PDE

DL kinetics: Numerical simulation (cont.)

[Fok, Rosales, DM, 2008]

Collapse of discrete simulation data for large t



ODE solution

PDE $\Longrightarrow$ ODE:

$$\left.\begin{array}{l} m = t^{-1/5}M(\xi)\ ; \quad \xi = xt^{-1/5} \\ \partial_t m = -\partial_x^4(m^2) \Rightarrow \dfrac{1}{5}(\xi M)' = (M^2)'''' \end{array}\right\}$$

Solved ODE numerically via:

Continuity of: slope, m; flux, $(m^2)_{xx}$; and height h at facet edges.

Speculated expansion:

$$M(\xi) = \sum_{n=1}^{\infty} A_n(\xi - \xi_f)^{n/2} \quad \left\{ \begin{array}{l} \text{Leading order: ``\textbf{local equilibrium}''} \\ \text{[Jayaprakash, Saam, Teitel, 1983; Bonzel 2003]} \end{array} \right.$$

How does this behavior *emerge* directly from steps?

Integral equation approach: DL kinetics

Proposition [DM, Nakamura, *preprint*] *Consider the self-similar slopes* $m_i(t) = t^{-1/5} M_i$ *under* **DL kinetics**. *Assume that, in the limit* $\epsilon \downarrow 0$, $M_i \to \tilde{m}(h)$. *Then,* $\tilde{m}(h)$ *satisfies the (nonlinear) integral equation*

$$\tilde{m}(h)^3 = C_1 h - C_2 \int_0^h \frac{z(h-z)}{\tilde{m}(z)}\, dz + \int_0^h \int_0^z \frac{(h-z)(z-\zeta)}{\tilde{m}(z)\tilde{m}(\zeta)}\, d\zeta\, dz \ ,$$

$0 < h < 1$; C_1, C_2 *are subject to* $\lim_{h\uparrow 1} \tilde{m}(h) = 0 = \lim_{h\uparrow 1} \tilde{J}(h)$ *(flux).*

Note on proof. Set $\psi_i = M_i^3$. Split difference scheme to **2nd-order scheme**:

$$\psi_{i+1} - 2\psi_i + \psi_{i-1} = -\frac{\epsilon^2 J_i}{\psi_i^{1/3}} \ , \quad J_{i+1} - 2J_i + J_{i-1} = -\frac{\epsilon^2}{\psi_i^{1/3}} \ ;$$

$i = 0, \ldots, N-1$ and J_i is discrete **flux**. *Terminating conditions:*

$$\psi_{-1} = 0 = \psi_N \ , \qquad J_{-1} = 0 = J_N \ .$$

Treat right-hand sides as forcings; solve exactly to obtain **sum equations**. Take limit $N \to \infty$ with $N\epsilon = 1$, $j\epsilon = O(1)$ (fixed height).

Integral equation approach: ADL kinetics

Proposition [DM, Nakamura, *preprint*] *Consider the self-similar slope* $m_i(t) = t^{-1/4} M_i$ *in ADL kinetics. Assume that, in the limit* $\epsilon \downarrow 0$, $M_i \to \tilde{m}(h)$*. Then, from discrete schemes* $\tilde{m}(h)$ *satisfies*

$$\tilde{m}(h)^3 = C_1 h - C_3 h^3 + \frac{1}{6} \int_0^h \frac{(h-z)^3}{\tilde{m}(z)}\, dz \ , \quad 0 < h < 1 \ .$$

The constants C_1, C_3 *are subject to* $\lim_{h\uparrow 1} \tilde{m}(h) = 0 = \lim_{h\uparrow 1} \tilde{J}(h)$.

Other approach: ADL case: Energy steepest descent

[Al Hajj Shehadeh,Kohn,Weare, *preprint*]

- *ODEs for* m_j*:* l^2*-steepest descent of discrete energy*
- *For monotone initial data, unique* $m_j(t)$ *exist globally*; $m_j(t) > 0$, $\forall\ t > 0$
- *The slope ODEs have a unique self-similar solution:* $m_j(t) = t^{-1/4} M_j$*. This is asymptotically stable*

An analogous approach to DL kinetics is currently elusive

Limit $N \to \infty$**:**

- Continuum slope $m(h,t)$; viewed as function of **height**, h
- *PDE with* $m = 0$ *at edges:* L^2*-steepest descent of energy functional*
- **Zero flux**, $(m^3)_{hh}$, *at facet edges* ($h = 0, 1$) *as natural boundary conditions*

Near-facet expansion (DL or ADL kinetics)

Formal expansions are derived by **iterations** of integral equations.
Near-facet expansion by one iteration with $\xi = t^{-\alpha}x$ $(\alpha = 1/5, 1/4)$:

$$\tilde{m}(h) = (C_1 h)^{1/3} + o(h^{1/3}) \quad \text{as } h \downarrow 0$$

$$\Rightarrow \quad \tilde{m}(h(\xi)) = \left(\frac{2}{3}\right)^{1/2} C_1^{1/2} \bar{\xi}^{1/2} + o(\bar{\xi}^{1/2}), \quad \bar{\xi} = t^{-\alpha}(x - x_f(t)) \to 0$$

Agreement with assumption for PDE numerics [Fok, Rosales, DM 2008]

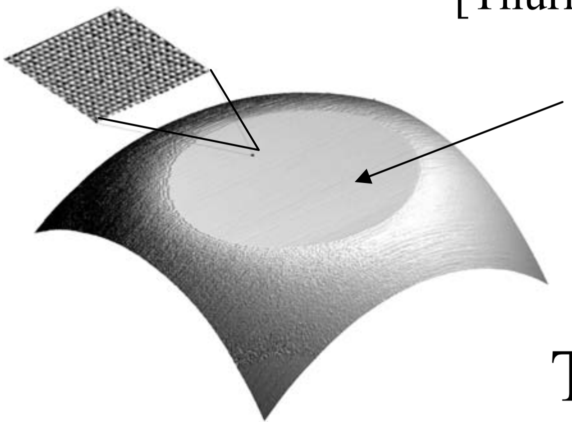
Agreement with thermodynamic equilibrium [Bonzel, 2003]

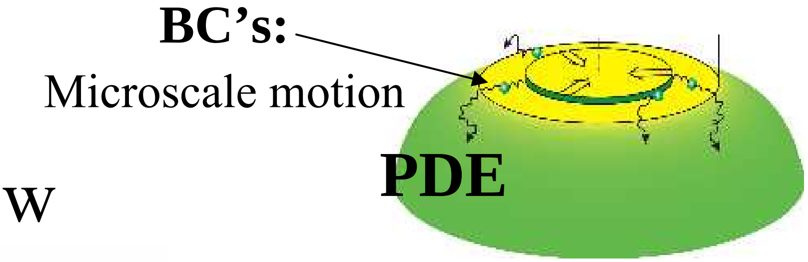
Radial case:
Microscale condition

Crystal surfaces have facets: Microstructure effect

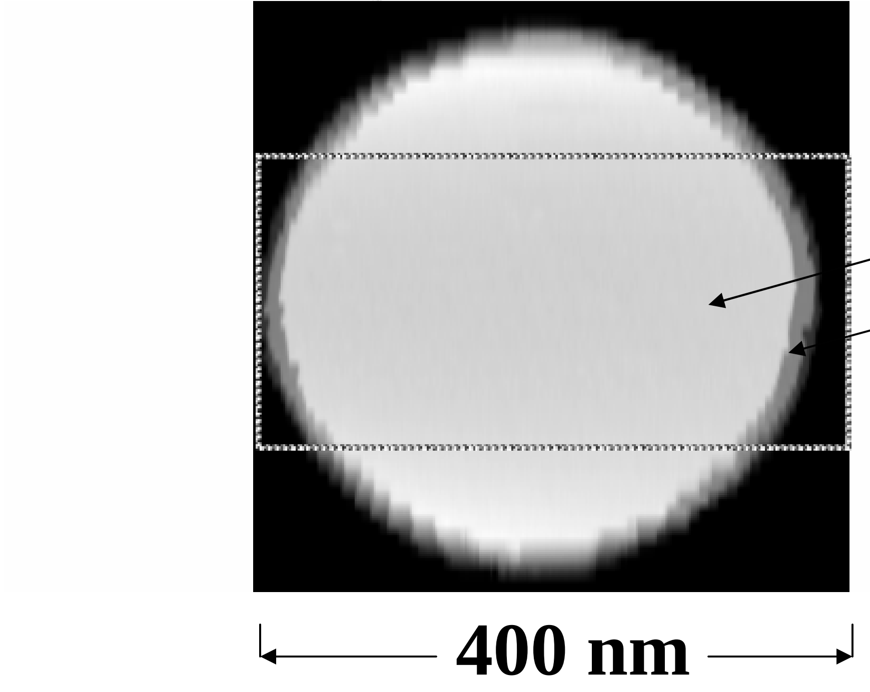
STM imaging from E. Williams: supported Pb crystallite, 353-423 K

[Thurmer, Reutt-Robey, Williams, Uwaha, Emundts, Bonzel, 2001]





Top view



Layers of atomic height:

Top layer

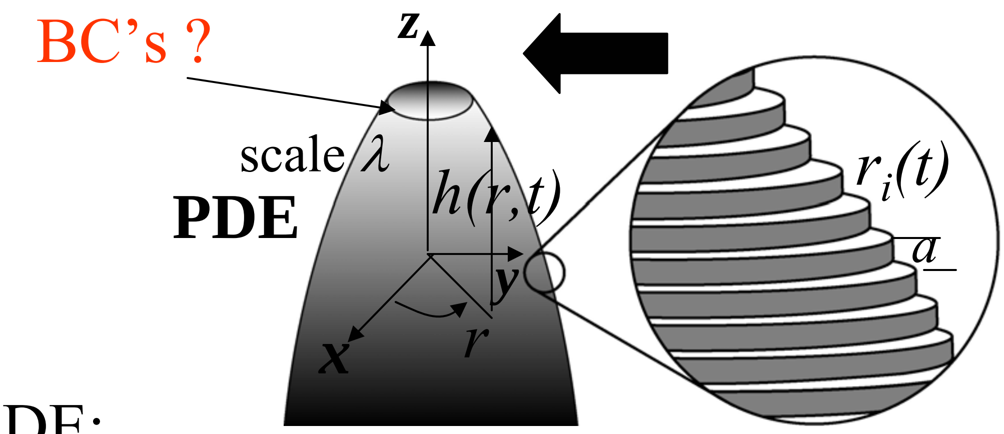
Next layer (grey)

Physically:

BC's at facet edge

must retain microscale details.

Issue of boundary conditions



DL kinetics:

$D_s/(ka) << 1$

PDE:

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

$$\boxed{\frac{1}{B}\frac{\partial h}{\partial t} = \frac{1}{r^3} \enclose{circle}{-g}\, \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial}{\partial r}\frac{1}{r}\frac{\partial}{\partial r}(rm^2)}$$

$$\enclose{circle}{g = g_3/g_1}$$

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

What are the "right" boundary conditions?

Discrete scheme:

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

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

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

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

entropic, elastic-dipole interactions

Fully continuum approach (neglecting microstructure)

$\frac{\delta E}{\delta h}$ is not defined locally across facets

PDE $h_t = \Delta(\delta E/\delta h)$ is replaced by the rule

$$\boxed{-h_t \quad \text{is element of } \underset{\text{subgradient}}{\partial_{H^{-1}} E[h]} \text{ with minimal } H^{-1} \text{ norm}}$$

$$\partial_{H^{-1}} E[h] := \left\{ f : E[g] - E[h] \geq \langle f, g-h \rangle_{H^{-1}} \quad \forall g \in H^{-1} \right\}$$

Recall: $\langle f, g \rangle_{H^{-1}} = \langle -\Delta^{-1} f, g \rangle_{L^2}$

Natural boundary conditions: continuity of slope, flux, chem. potential

[Kashima, 2004; Odisharia, 2006]

Choices of boundary conditions

``Natural'' (Thermodynamic) BC's
(via subgradient formulation)

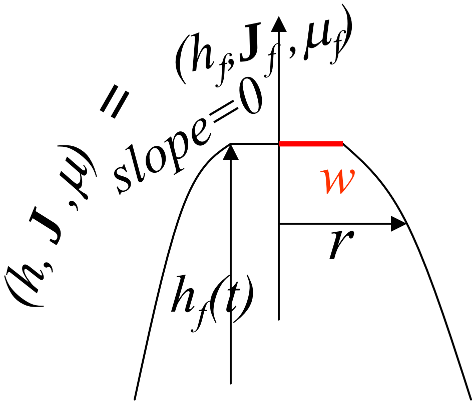
- Height continuity, $h(w,t)=h_f(t)$
- **Slope continuity**
- Flux continuity, $\boldsymbol{J}=\boldsymbol{J}_f$

μ : `step chemical potential' outside facet

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

- μ is extended **continuously** on facet

replace



[Spohn, 1993; Shenoy, Freund, 2002; Kashima, 2004; DM, Aziz, Stone., 2004-05]

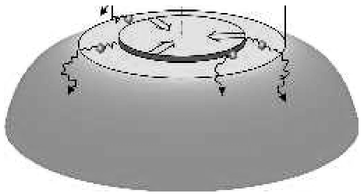
``Facet drop'' (fdr) condition:

- Same

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

time of
nth step collapse

step height



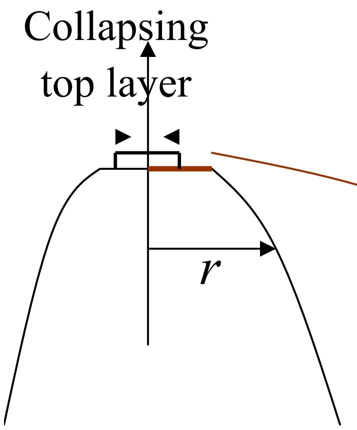
Need to know times t_n

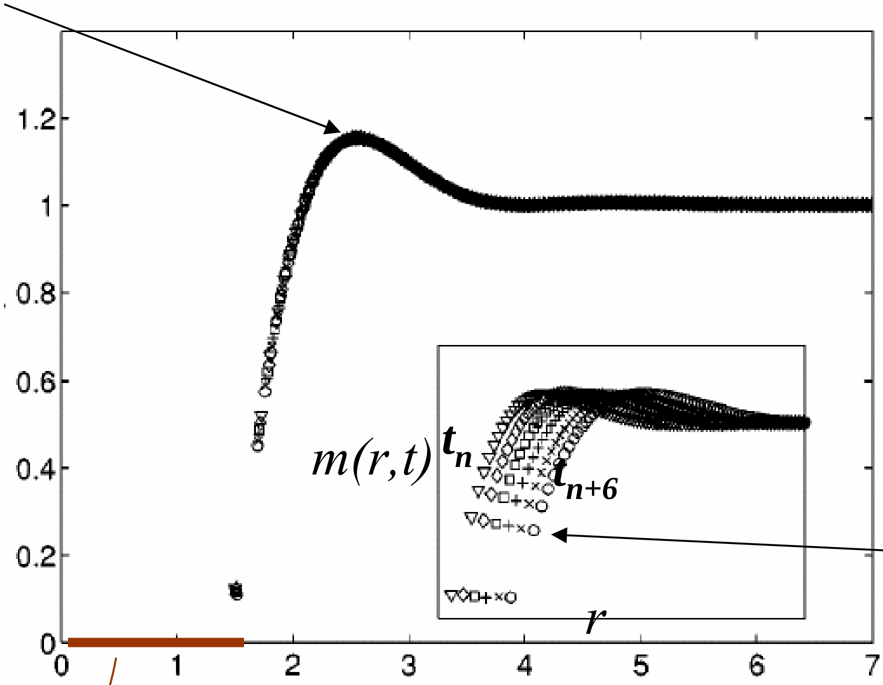
[Israeli, Kandel, 1999;
DM, Fok, Aziz, Stone, 2006]

Solving step equations: Self-similar solutions for long *t*

Data **collapse**;
initial cone

$m=\Lambda(\chi)$





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

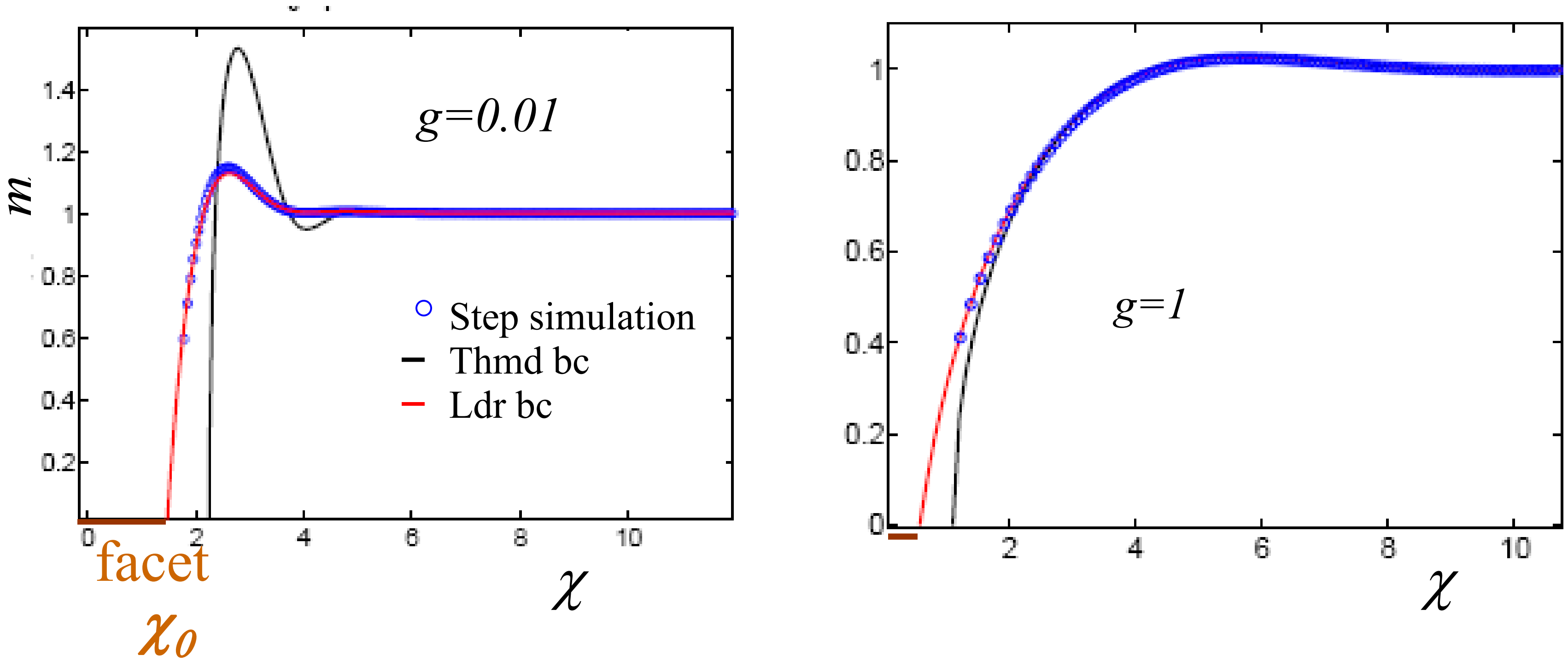
Data:
Numerical
simulations
of step motion

$$\text{Collapse times:} \qquad t_n \sim t^* \cdot n^q, \quad n >> 1$$

[Cone: Israeli, Kandel, 1999; Other shapes: Fok, 2006]

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

Continuum needs parameter t^* (from discrete eqs)



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

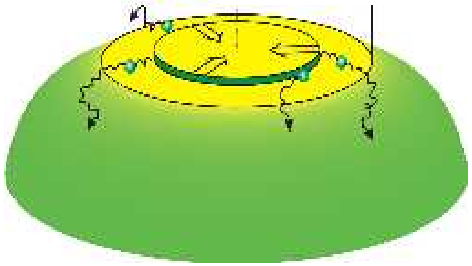
[DM, Fok, Aziz, Stone, 2006]

Radial case:
Facets and shocks
in full continuum

Numerical simulations for weak step interactions

Simulations for **infinite** initial cone

DL kinetics

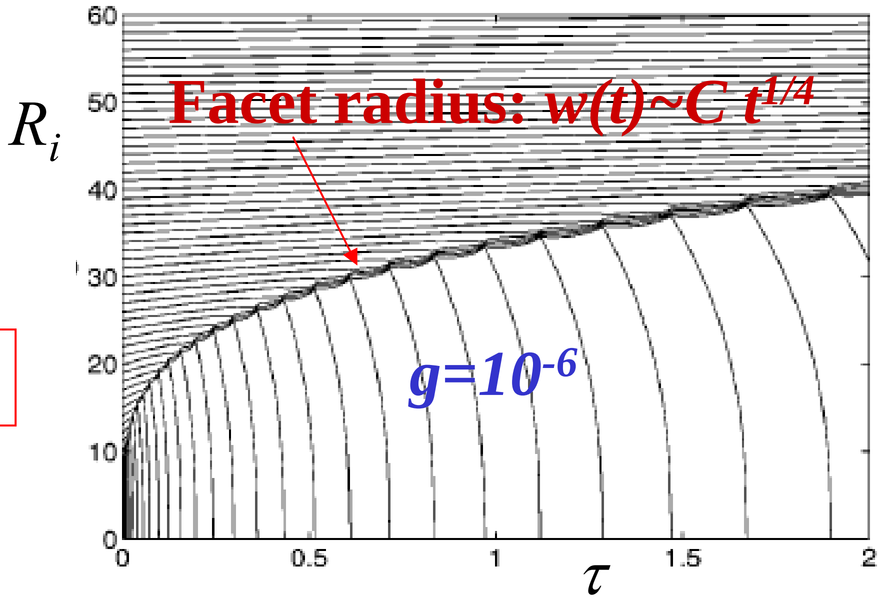


Special bunch: Steps near facet

Step density becomes self-similar

Top step collapse times: $t_n \sim t^* \cdot n^q$

[Israeli, Kandel, 1999; Fok, 2006]

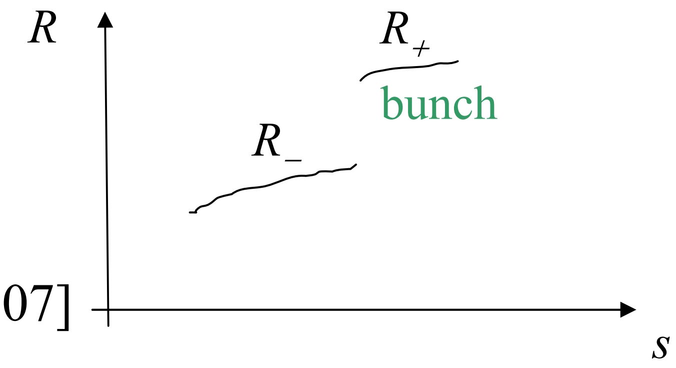


In Lagrangian variables, step bunches resemble ``shock-wave type solutions''

R: scaled step position

s: scaled step number, or height

[Fok, Rosales, DM, 2007]

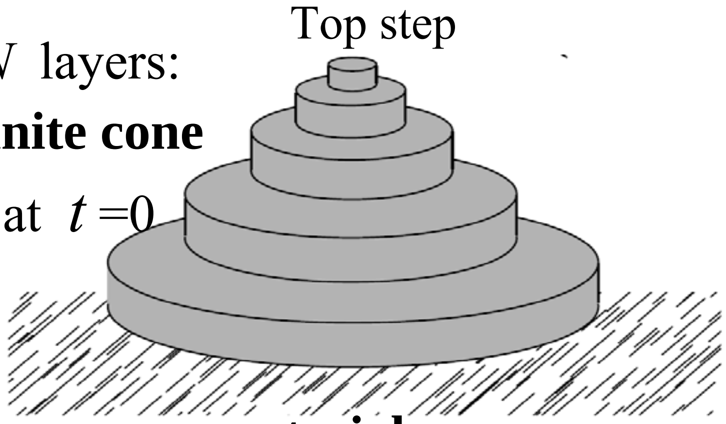


Finite structure [Fok, Rosales, DM, 2008]

N layers:

Finite cone

at $t=0$



same material

- Diffusion-limited (DL) kinetics
- Bottom step: perfect sink

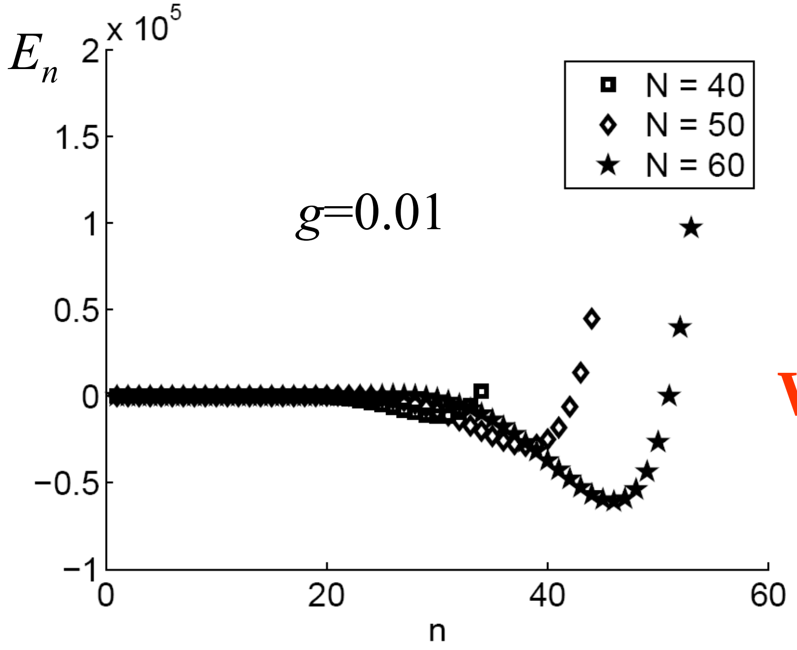
No self-similarity for step density

Define:

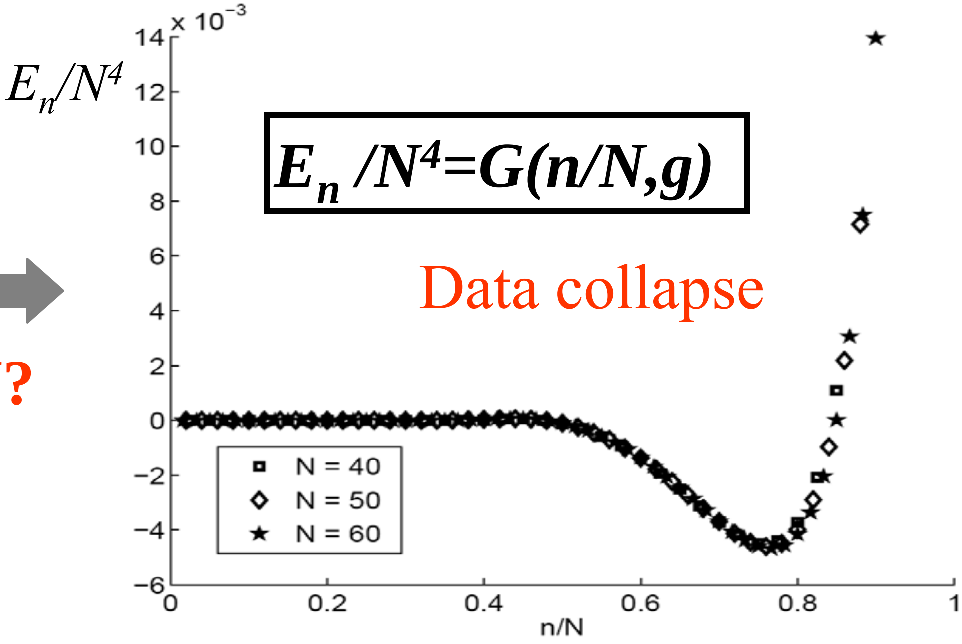
$$\boxed{E_n(N,g) := t_n(N,g) - t_n(\infty,g)}$$

$\sim t^* n^4$

Collapse time of nth step



WHY?



$$\boxed{E_n/N^4 = G(n/N,g)}$$

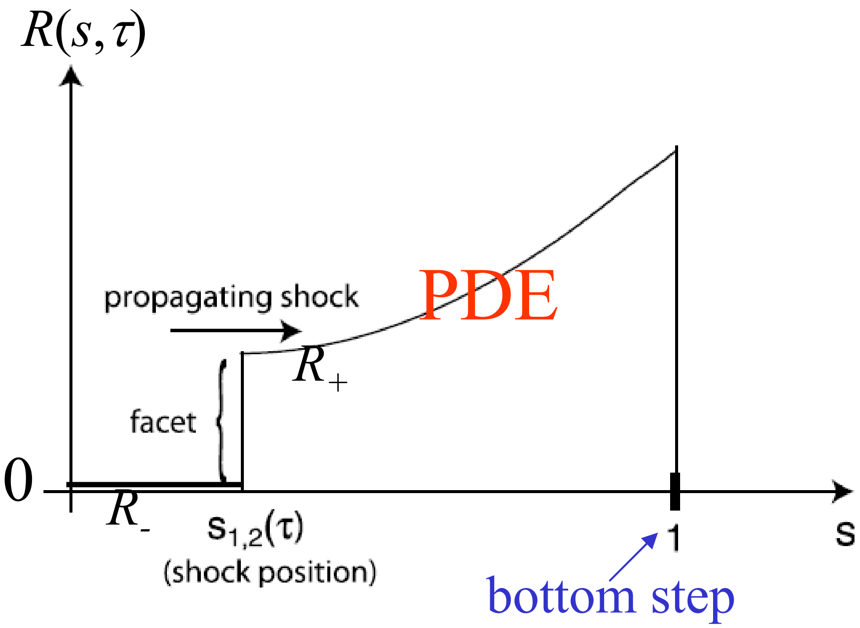
Data collapse

Continuum treatment, $g \ll 1$ (weak interactions)

PDE: $$R_\tau = -\frac{1}{R}\left\{\frac{1}{R} + \frac{3g}{R_s}\left[\xcancel{\frac{1}{2RR_s} + \left(\frac{RR_{ss}}{R_s^4}\right)_s}\right]_s\right\} \qquad s = n\varepsilon = n/N$$

For $g=0$, PDE allows for propagation of discontinuities:``shock waves''

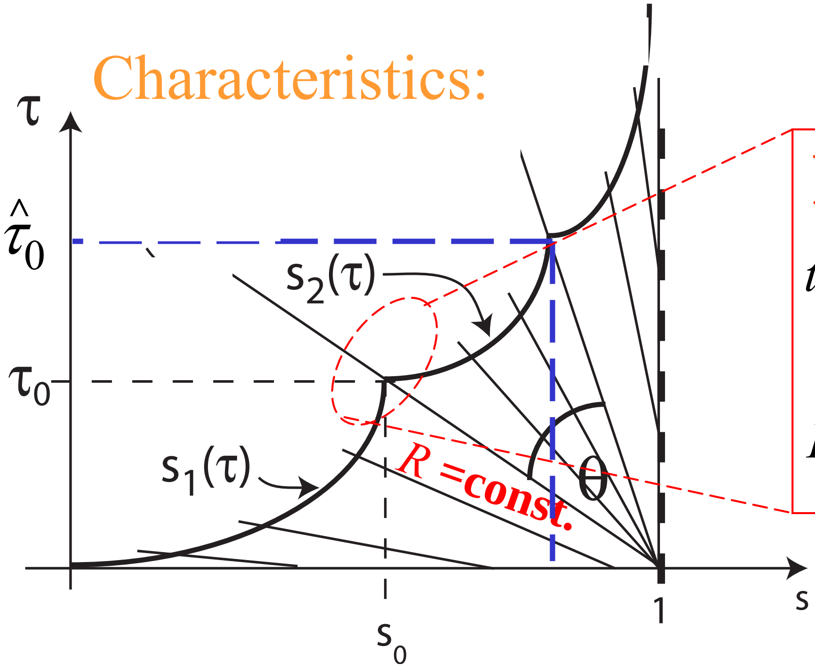
Shocks correspond to facets



Shocks are also introduced for kinem. eq. for **density** of 1D step flow in [N. Cabrera, D.A. Vermilyea, 1958;F.C. Frank, 1958]

Collapse times of step on top of facet

Characteristics:

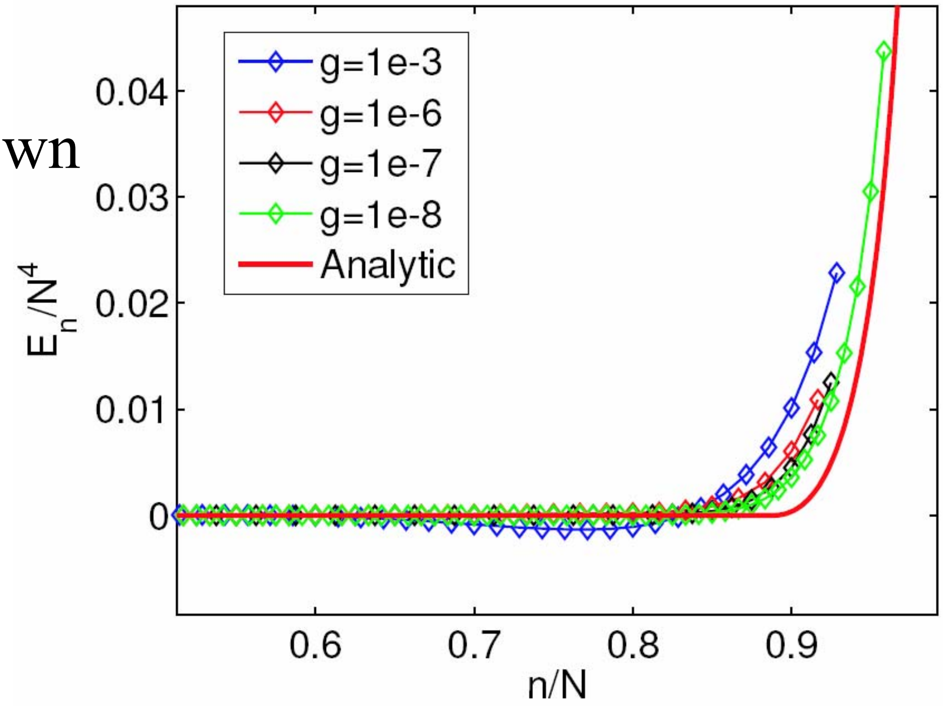


$s_{1,2,3}(\tau)$: known ↔ $\tau(s)=t_n$: known

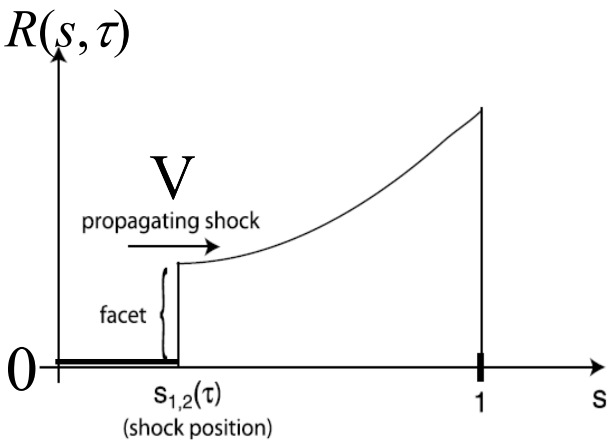
Result:

$$t_n(g \to 0)/N^4 = \begin{cases} T^*(n/N)^4, & n/N < 8/9 \\ \sqrt{\dfrac{B}{1-n/N}}, & 8/9 < n/N < \tilde{s}_0 < 1 \end{cases}$$

$$B = 3^{-6}, \quad T^* = (3/4)^6$$



Elements of Derivation



PDE is recast to conservation law:

``density''   ``flux''

$$\boxed{\phi_\tau + q_s = 0}$$

Choose $\phi = R^2$, $q = 2/R$

Valid **right** (+) of shock

No PDE description **left** (-) of shock

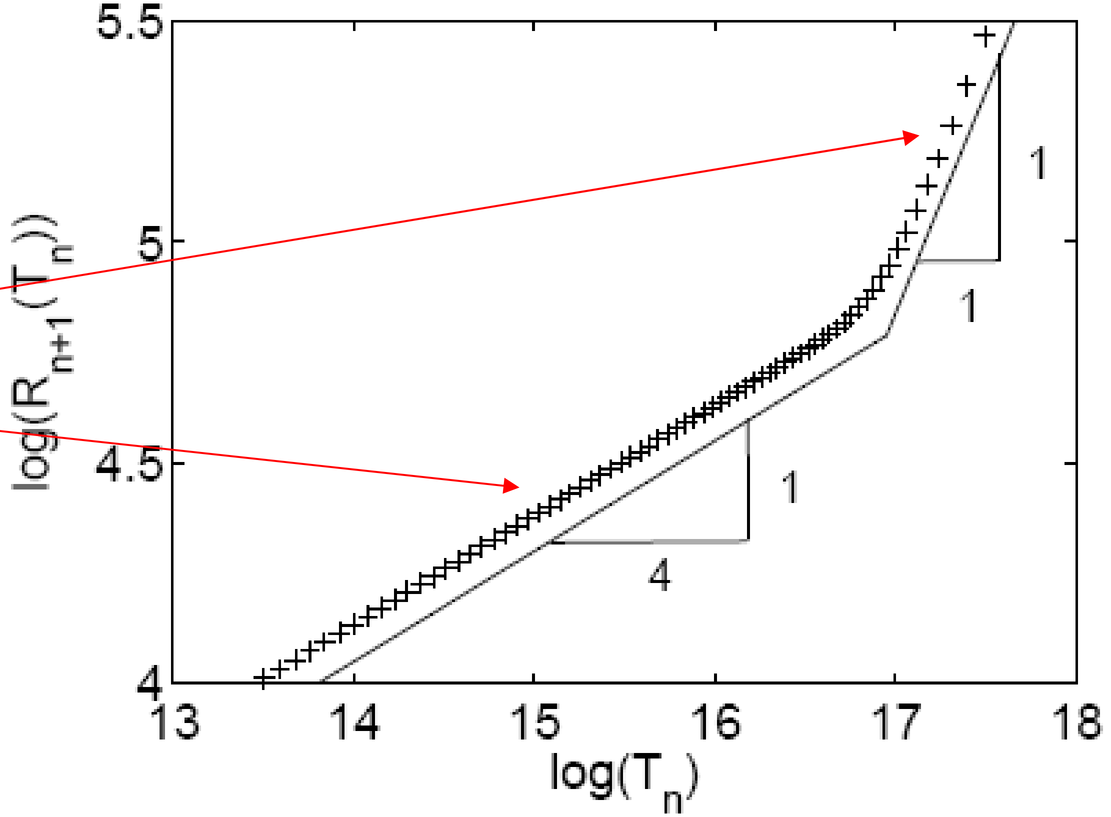
Shock velocity V is expressed
by **Rankine-Hugoniot** condition

$$V = [q] \,/\, [\phi]$$

Jump in q: $q_+ - q_-$

Take $q_- = 0 = \phi_-$

Switch in time behavior of facet radius, $R_{\mathrm{f}}(t)$:



$$R_{\mathrm{f}}(t) \sim B^{-1/3} t$$

$$R_{\mathrm{f}}(t) \sim \sqrt{3}\, t^{1/4}$$

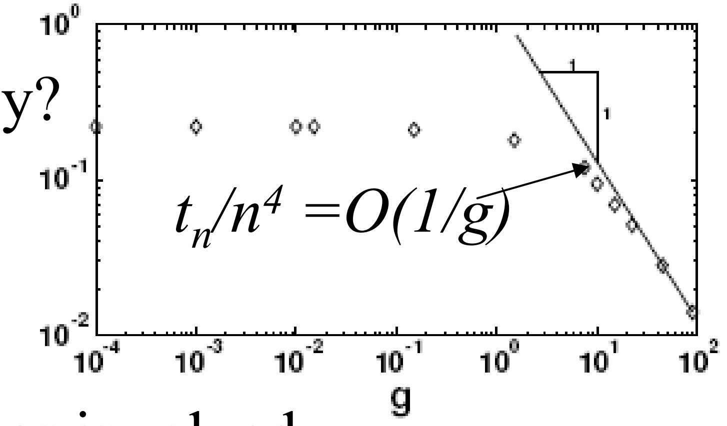
Crystal facets & continuum: Summary

- Step schemes not consistent with continuum near facets

Special case: semi-infinite facets; some rigorous results in ADL regime

- Free-boundary problem: Boundary conditions require parameters (collapse times, t_n) from discrete scheme.
- Subgradient formulation: formal H^{-1} viewpoint is **not** step-consistent

- May t_n be evaluated/estimated analytically? Possibly, if $g >> 1$ or $g << 1$



$t_n/n^4 = O(1/g)$

- Because of nonlinearity and high derivatives involved, slope profile is **very sensitive** to input t_n . Alternate formulation ?

Experiment escorts us last -
His pungent company
Will not allow an Axiom
An Opportunity

Emily Dickinson (1830-1886)