

Wetting and dewetting of solid films

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- 1 Static Wetting of liquids and Solids
- 2 Dynamics of wetting
- 3 Consequences of singular anisotropy
 - Experimental evidences
 - 2D SOS KMC
 - Dewetting of thin films: KMC vs model
- 4 Wetting potential
 - Mesoscopic Continuum thin film model
 - Derivation of the TL Boundary Condition
 - Accelerated mass shedding
 - KMC study of magic heights
 - Conclusion
- 5 Immersed solids
 - Introduction
 - Thin film model
 - Pressure solution
 - Growth: cavity formation
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Wetting and dewetting of liquid and solid films

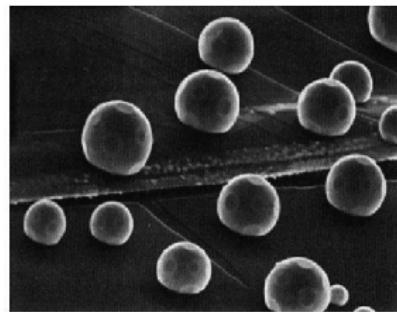
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Some examples



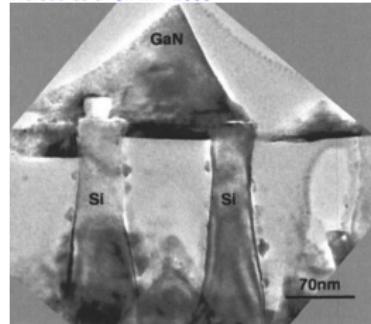
Au/Graphite

J.-J. Métois



GaN on Si nano-pillars

Hersee et al J.A.P. 2005



Equilibrium shape, Wulff 1901, Kaishev 1950

J.-J. Métois, Au/Graphite

Free energy

$$\mathcal{F} = \int_{VS} ds \gamma_{VS}(\theta) + \int_{SA} ds \gamma_{SA}(\theta) + \int_{AV} ds \gamma(\theta)$$

Total number of atoms

$$\mathcal{N} = \Omega^{-1} \int \int_{\mathcal{D}} d^2 r$$

Minimal shape: $\delta(\mathcal{F} - \mu\mathcal{N}) = 0$

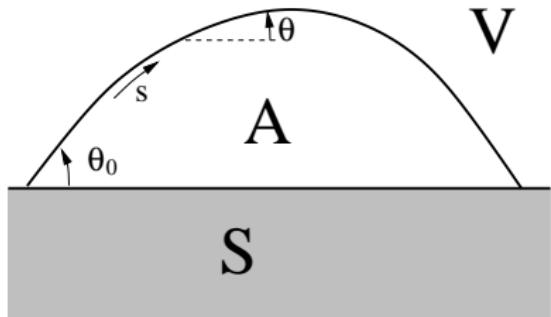
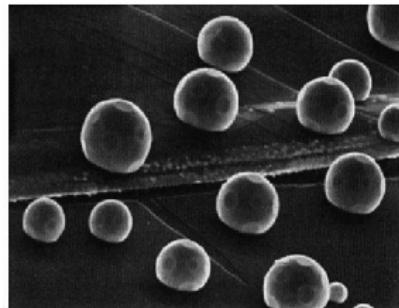
Equilibrium Equations

$$\Delta = \gamma_{VS} - \gamma_{SA}$$

$$\text{Stiffness } \tilde{\gamma}(\theta) = \gamma(\theta) + \gamma''(\theta)$$

$$\text{Wulff : } \mu = \Omega \tilde{\gamma}(\theta) \kappa$$

$$\text{Young : } \Delta = \gamma(\theta_0) \cos(\theta_0) - \gamma'(\theta_0) \sin(\theta_0)$$



Isotropic

Isotropic solid $\gamma(\theta) = \bar{\gamma}$

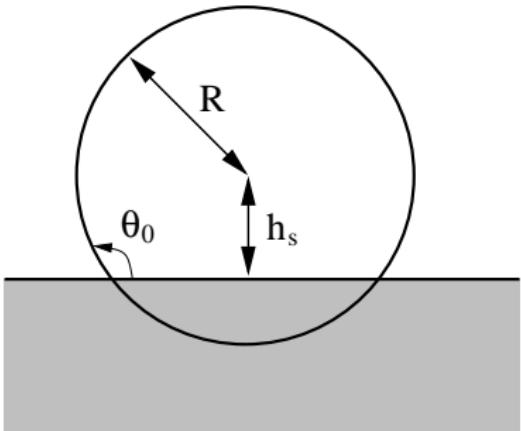
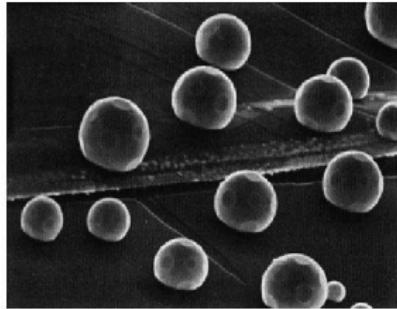
$$\mu = \Omega \bar{\gamma} \kappa \quad \Rightarrow \quad R = \frac{\Omega \bar{\gamma}}{\mu}$$

$$\bar{\gamma} \cos(\theta_0) = \Delta \quad \Rightarrow \quad h_s = -\frac{\Omega \Delta}{\mu}$$

μ fixed from $\mathcal{N} = (\theta_0 - \sin[2\theta_0]/2)R^2/\Omega$

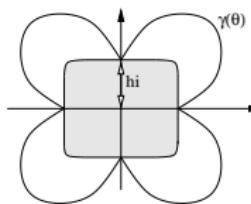
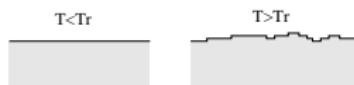
Transition:

Partial wetting \rightarrow complete wetting
when $h_s \rightarrow -R$, i.e. $E_S = \Delta + \bar{\gamma} \rightarrow 0$

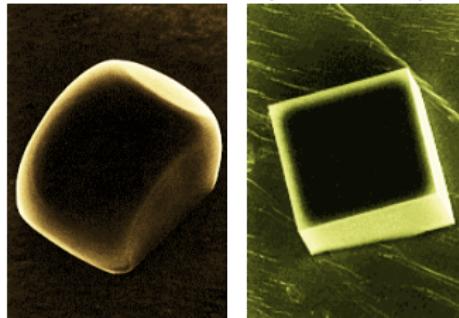


Facets

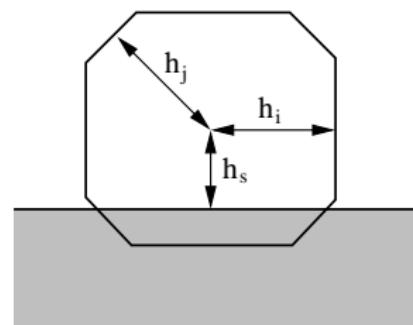
Roughening temperature T_r



NaCl, Métois et al (620-710°C)



For usual crystals $T_r \sim T_M$



$$h_i = \frac{\Omega \gamma_i}{\mu}$$

$$h_s = \frac{\Omega \Delta}{\mu}$$

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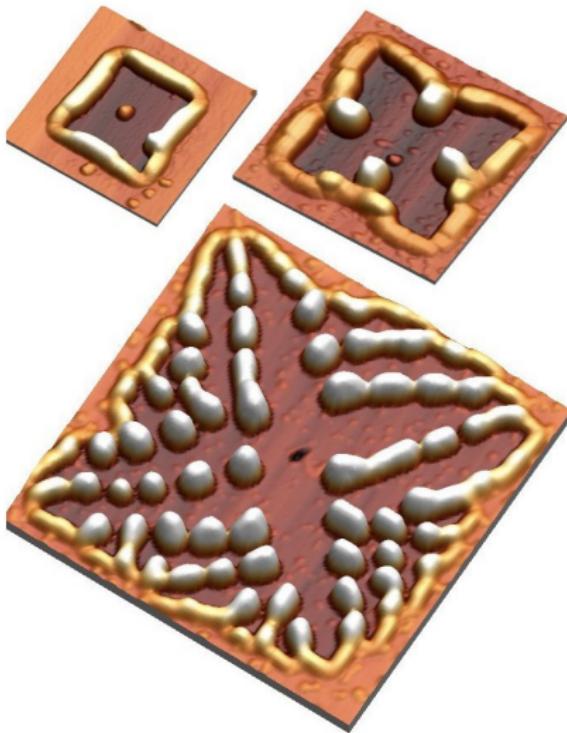
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Dewetting experiments: surface diffusion + anisotropy

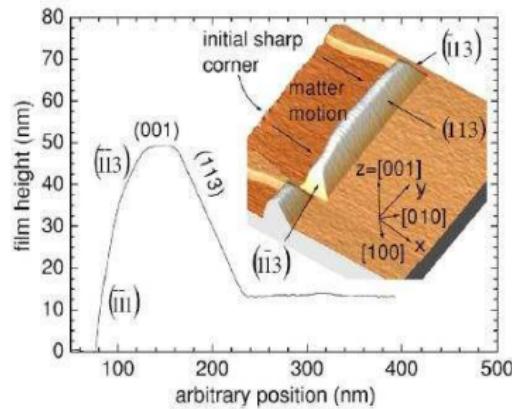
Experiments SOI: Si(100)/a-SiO₂

P. Müller et al Cinam Marseille



SOI (Si/SiO₂), AFM

Dornel Barbe Crecy Lacolle Eymery PRB2006



Surface Diffusion Mullins' Model

Local chemical potential $\mu = \Omega \tilde{\gamma} \kappa$.

Mullins model:

$$\begin{aligned} j &= -\frac{Dc}{k_B T} \partial_s \mu \\ v_n &= -\Omega \partial_s j \end{aligned}$$

Triple Line

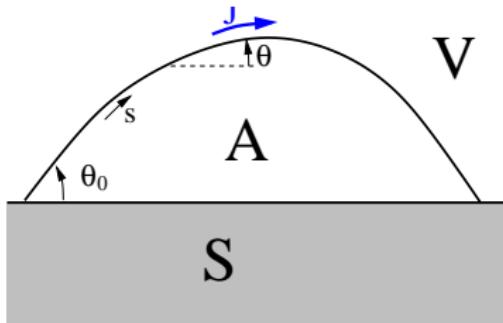
Equilibrium contact angle $\theta = \theta_0$

Linear perturbations $h = h_* + \delta h$

$\partial_t \delta h \sim \partial_{xxxx} \delta h$

Relaxation time of small perturbations

$t \sim L^4$



Liquid-state Dewetting

Polymer film (PDMS/Si)

G. Reiter et al PRL2000.2001, Fetzer et al

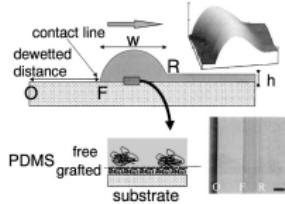


FIG. 1. Schematic representation of the experimental setup. A typical shape of the rim, as measured by atomic force microscopy, is shown in the upper right corner. The size of the image is $60 \times 60 \times 0.4 \mu\text{m}^3$. Note that the lateral scale is about a factor of 100 larger than the vertical scale. In the lower right corner we show an optical micrograph representing the top view corresponding to the scheme. The length of the bar equals $50 \mu\text{m}$.

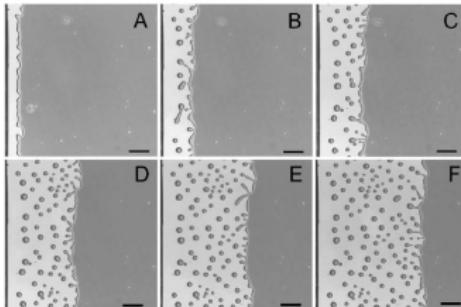
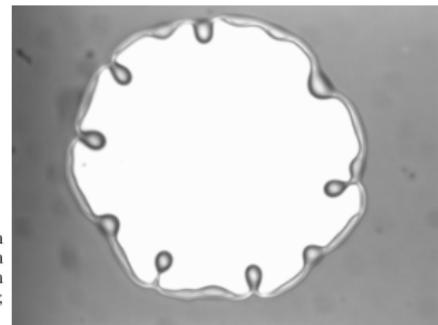


FIG. 2. Typical optical micrographs for the droplet formation at the later stages of the retraction of a 90 nm thin PDMS film ($1000 \text{ Pa} \cdot \text{s}$) at 130°C on a silicon wafer coated with a 6 nm grafted PDMS layer for A: 60; B: 190; C: 310; D: 510; E: 690; and F: 870 sec, respectively. The length of the bar is $100 \mu\text{m}$.



Liquids: viscosity and substrate friction

Viscous dissipation under shear $\dot{\gamma} = \partial_y v_x + \partial_x v_y$

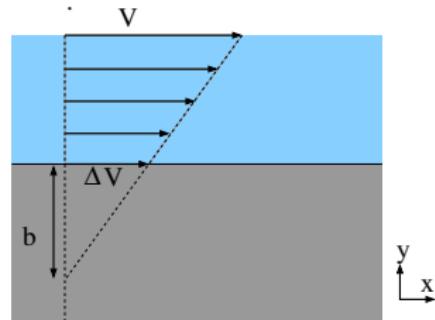
$$dQ \sim \eta \dot{\gamma}^2 dV$$

Continuity of tangential stress [Navier 1823](#)

$$\eta \partial_y v|_{wall} = \lambda \Delta v \rightarrow \Delta v = b \partial_y v|_{wall}$$

Slip length

$$\ell_s = \frac{\eta}{\lambda}$$



ℓ_s is usually small!

Link to wetting: hydrophobic \Rightarrow depletion $\Rightarrow b$ increases

$$\ell_s \sim (1 + \cos \theta)^{-2}$$

[D. M. Huang, et al Phys. Rev. Lett. 101, 226101 \(2008\)](#)

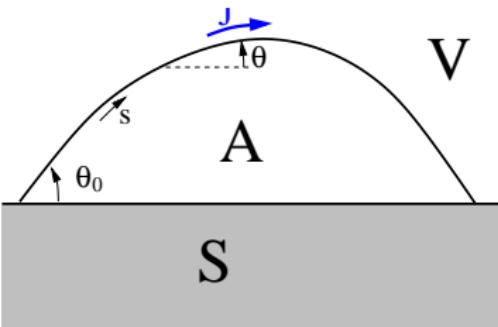
at max tens of nm for water on atomically flat hydrophobic surfaces

Hydrodynamics, lubrication Model

Local pressure variation $\Delta p = \tilde{\gamma} \kappa$.

Lubrication Model $\partial_x h \ll 1$, viscosity η , slip length ℓ_s

$$\begin{aligned} j &= -\frac{1}{\eta\Omega}(h^3/3 + \ell_s h^2)\partial_x\Delta p \\ \partial_t h &= -\Omega\partial_x j \\ \partial_t h &= -\frac{\gamma}{\eta}\partial_x[(h^3/3 + \ell_s h^2)\partial_{xxx}h] \end{aligned}$$



Triple Line

Equilibrium contact angle $\theta = \theta_0$

Linear perturbations $h = h_* + \delta h$

$$\partial_t \delta h \sim \partial_{xxxx} \delta h$$

Relaxation time of small perturbations

$$t \sim L^4$$

Generalized Model predictions 1D & small slopes

$$\partial_t h = \partial_x [h^n \partial_{xxx} h]$$

Scaling $\theta \ll 1$

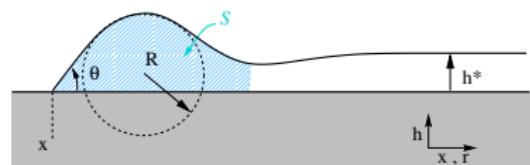
$$\partial_{xx} h \sim \frac{1}{R} \quad h \sim R\theta^2 \quad x \sim R\theta$$

Triple line velocity

$$v = \frac{1}{\theta} \partial_t x_0 = \frac{1}{\theta} \partial_x [h^n \partial_x \frac{1}{R}] \sim \frac{\theta^{2n-3}}{R^{3-n}}$$

Mass conservation

$$\begin{aligned} \partial_t \mathcal{S} = vh^* &\rightarrow \theta^3 \partial_t R^2 \sim \frac{\theta^{2n-3}}{R^{3-n}} h^* \\ \mathcal{S} &\sim hL \sim R^2 \theta^3 \end{aligned}$$



Asymptotic scaling

$$\begin{aligned} R &\sim \theta^{-2(3-n)/(5-n)} h_*^{1/(5-n)} t^{1/(5-n)} \\ x_0 &\sim \theta^{(3+n)/(5-n)} h_*^{-(3-n)/(5-n)} t^{2/(5-n)} \end{aligned}$$

Multi-scale expansion / Example: $n = 0$, solid-state dewetting

Wong, Vorrhees, Miskis, Davis (2000)

small slope limit $\partial_x h \ll 1$

Mullins model

$$\begin{aligned}\partial_t h &= -\partial_{xxx} h \\ h(x_0(t)) &= 0, \quad \partial_x h = \tan \theta = \alpha, \quad \partial_x^3 h(x_0(t)) = 0, \quad h(x \rightarrow \infty) = 1.\end{aligned}$$

normalized variables

$$X = \alpha(x - x_0(t)), \quad Y = h, \quad T = \alpha^4 t, \quad b = \alpha^{-3} \frac{dx_0}{dt}.$$

Boundary conditions

$$Y(X = 0) = 0, \quad \partial_X Y(X = 0) = 1, \quad \partial_X^3 Y(X = 0) = 0, \quad Y(X \rightarrow \infty) = 1.$$

Slow dynamics $Y = Y_0 + Y_1 + Y_2 + \dots$, with $Y_{n+1} \ll Y_n$

$$\begin{aligned}\partial_X^4 Y_0 - b^3 \partial_X Y_0 &= 0 \\ \partial_X^4 Y_n - b^3 \partial_X Y_n &= -\partial_T Y_{n-1}\end{aligned}$$

Solve Y_n order by order and then impose no-flux condition

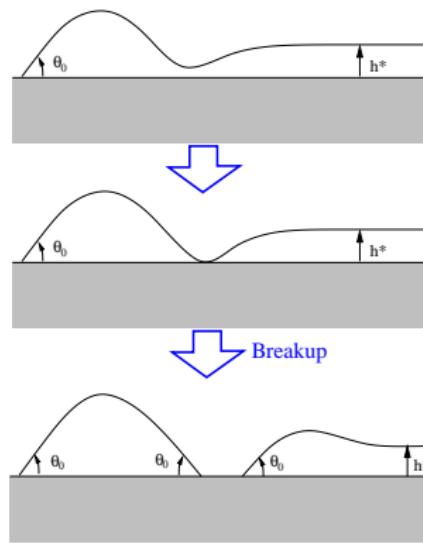
$$x_0(t) = \alpha \left(\frac{5t}{2\alpha} \right)^{2/5} - \frac{5}{4} \left(\frac{5t}{2\alpha} \right)^{1/5} + \dots$$

Multi-scale expansion / Example: $n = 0$, solid-state dewetting

Asymptotic scaling

$$\begin{aligned} R &\sim \theta^{-6/5} h_*^{1/5} t^{1/5} \\ x_0 &\sim \theta^{3/5} h_*^{-3/5} t^{2/5} \end{aligned}$$

Mass shedding Wong, Vorhees, Miskis, Davis (2000)



Multi-scale expansion / Example: $n = 2, 3$, liquid-state dewetting

Asymptotic scaling $n = 2$

$$R \sim t^{1/3}$$

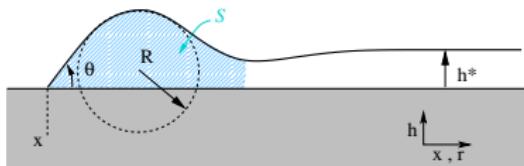
$$x_0 \sim t^{2/3}$$

Asymptotic scaling $n = 3$

$$R \sim t^{1/2}$$

$$x_0 \sim t$$

No Mass shedding!



Rim instability

$$\partial_t h = \nabla \cdot [h^n \nabla \Delta h]$$

Transversal direction y , perturbation $q = 2\pi/\lambda$

Assuming $y \sim x$

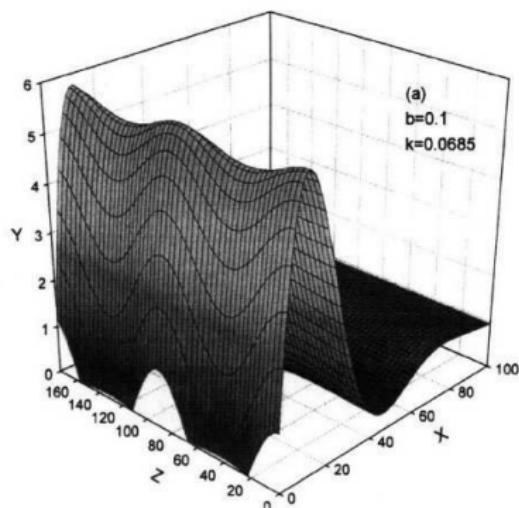
$$\rightarrow q \sim \frac{1}{\theta R} \sim \frac{1}{\theta^{(n-1)/(5-n)} h_*^{1/(5-n)} t^{1/(5-n)}}$$

$$n=0 \rightarrow \lambda \sim t^{1/5}$$

$$n=2 \rightarrow \lambda \sim t^{1/3}$$

$$n=3 \rightarrow \lambda \sim t^{1/2}$$

OPL 2013, Münch-Wagner 2014



Final finger wavelength?

Kan, Wong J.Appl. Phys. 2005

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Evidences of facets on the rim

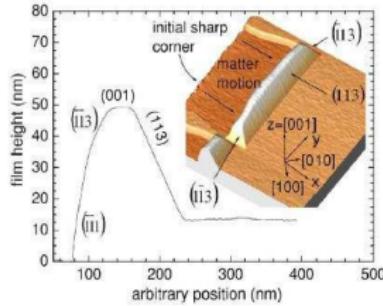
Ni(110)/MgO

J. Ye and C.V. Thompson, *Acta Materialia* 59, 582 (2011).



SOI (Si/SiO₂), AFM

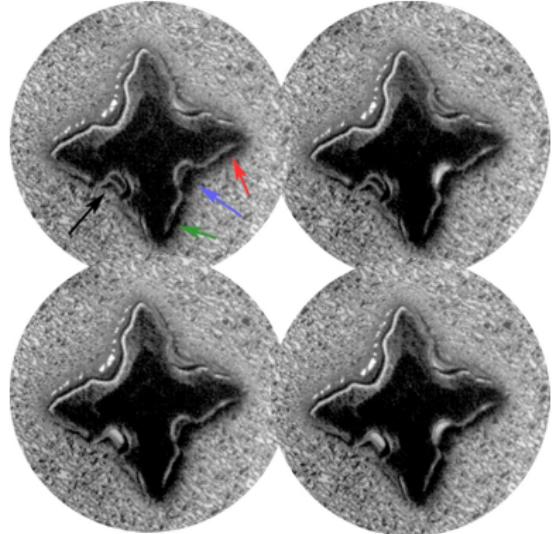
Dornel Barbe Crecy Lacolle Eymeric PRB2006



DEWETTING WITH FACETS?

SOI (Si/SiO₂), LEEM

E. Bussman et al, *New J. Phys.* 2011



Nucleation barrier

Dynamics limited by peeling or nucleation

Combe, Jensen, Pimpinelli, Phys Rev Lett 2000

Mullins and Rohrer, J. Am. Ceram. Soc. 2000

Cost: $2\pi\rho\gamma_{step}$

Gain: $\pi\rho^2\Delta\mu$ per atom, with $\Delta\mu = E_S/h$

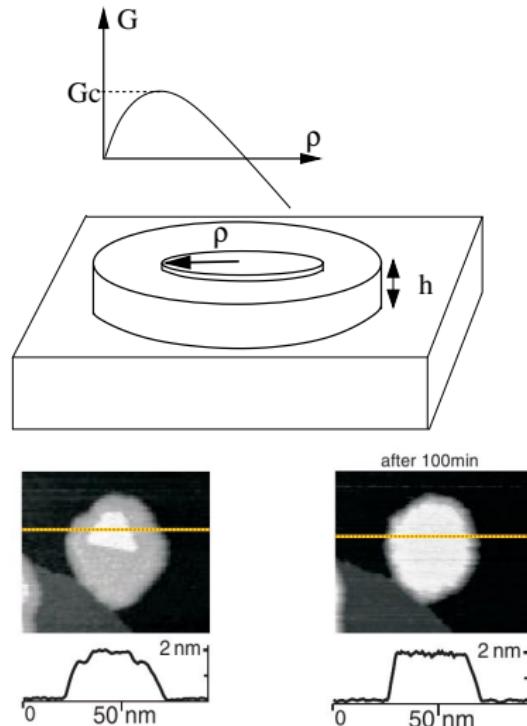
Total:

$$G = \gamma_{step}2\pi\rho - \frac{E_S}{\Omega h}\pi\rho^2$$

$$G_c = \Omega\pi \frac{\gamma_{step}^2 h}{E_S}$$

$$\mathcal{I} = \rho_0 \Gamma_{+c} \left(\frac{-a^4 \partial_{ss} G_c}{2\pi T} \right)^{1/2} e^{-G_c/T},$$

Slow relaxation time $t \sim e^{G_c/k_B T}$



Experiments Ice/Pt(111)

Thurmer, Bartelt P.R.L. 2008

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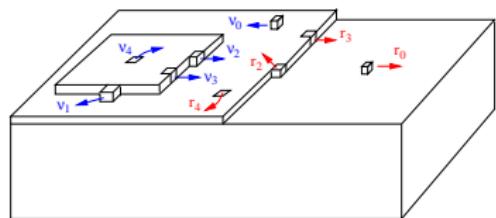
SOS KMC model

KMC simulations SOS Hopping rates

$$\text{A/S: } r_n = \nu_0 e^{-nJ/T + E_S/T}$$

- A/A: $\nu_n = \nu_0 e^{-nJ/T}$

J bong energy; E_S substrate contact energy ($= \Delta + \gamma_{100}$)



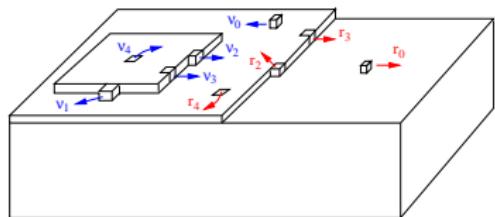
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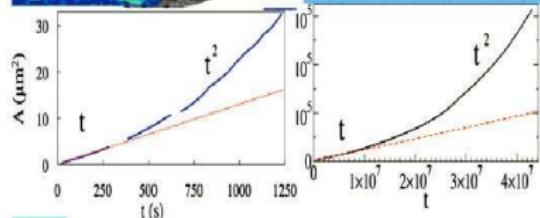
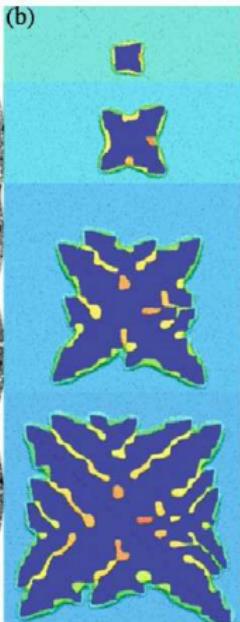
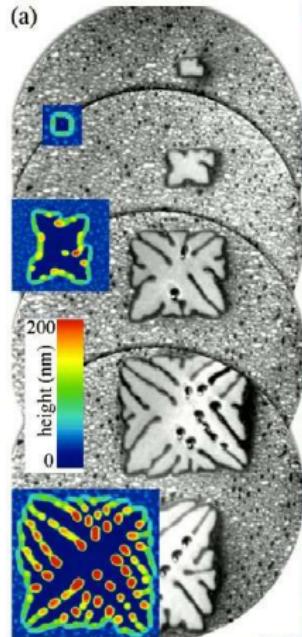
J bond energy; E_S substrate contact energy ($= \Delta + \gamma_{100}$)



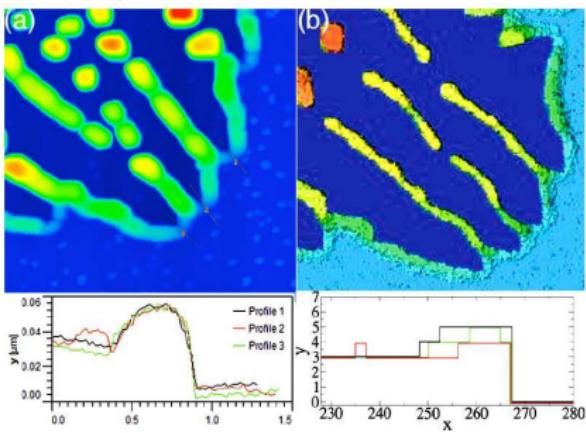
Equilibrium shape Low temperatures:

- $h = E_S^{2/3} J^{-2/3} N^{1/3}; h/L = E_S/J$
 $E_S = 1, N = 900, \rightarrow h = 8.7$, simul at $T/J = 0.35$

KMC vs SOI



$$h = 3, E_S = 1, T = 0.5$$

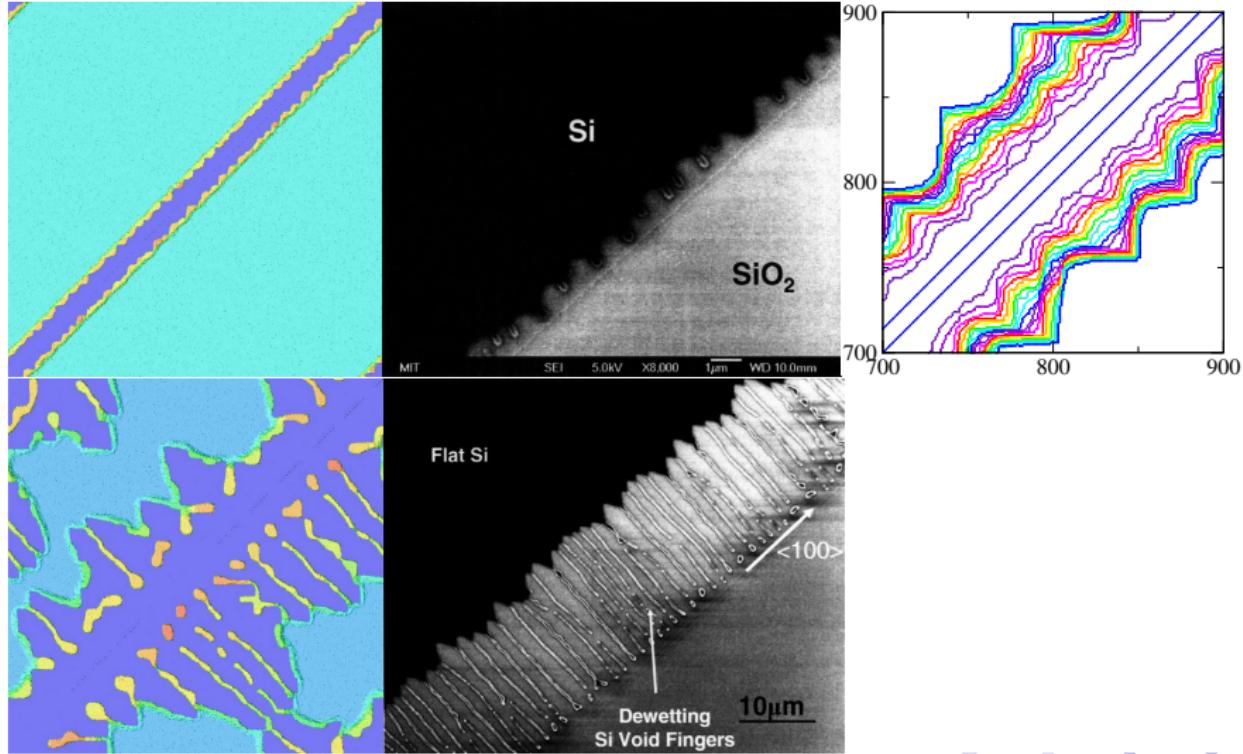


SOI system LEEM Experiments:
 E. Bussman, F. Leroy, F. Cheynis, P. Müller

11 fronts

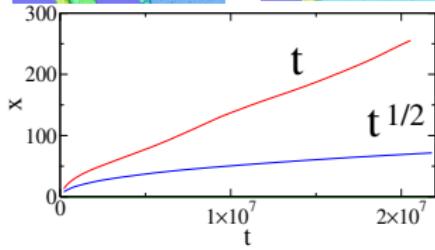
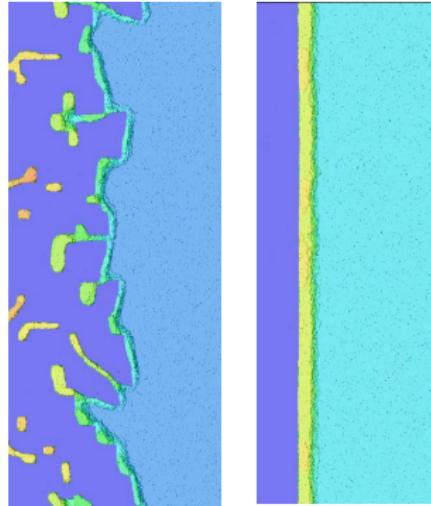
$h = 3, h_1 = 9, T = 0.5, E_S = 1.5,$

Danielson PhD Thesis, MIT 2008

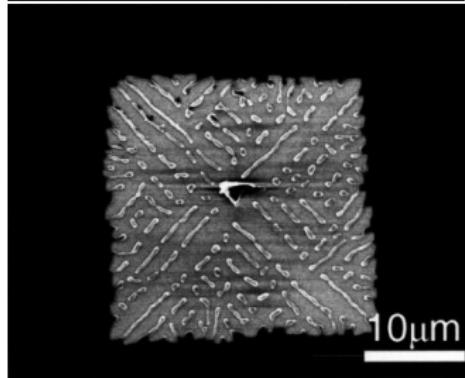
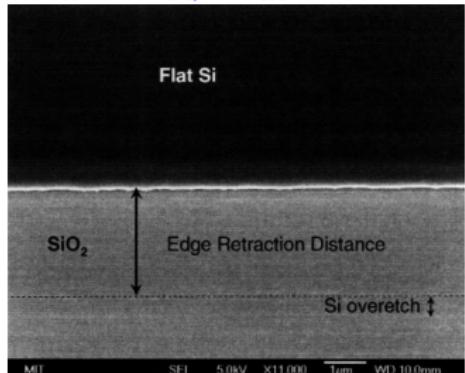


10 fronts: Metastability?

KMC

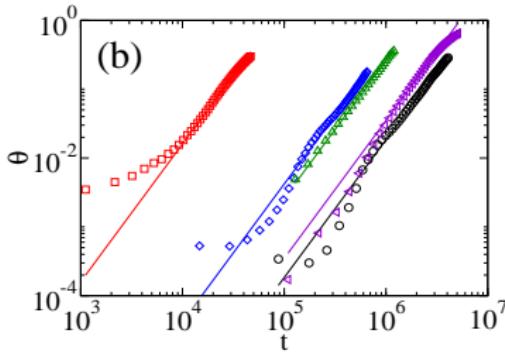
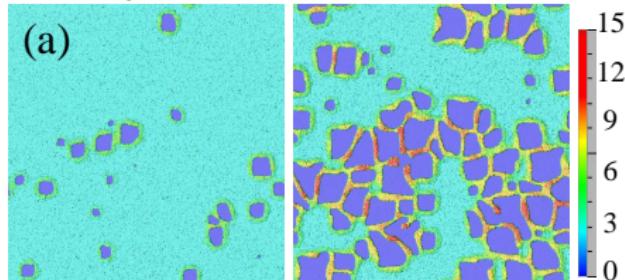


Danielson PhD Thesis, MIT 2008



Dewetting of a complete film

$h = 3, E_S = 0.7, T = 0.5$

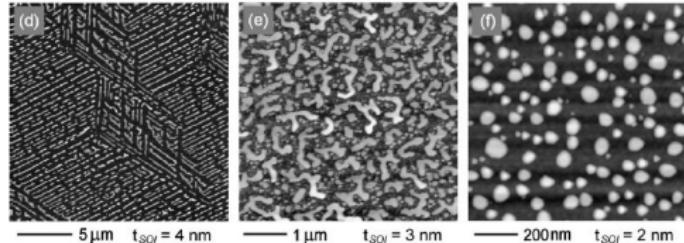


$$\text{hole radius } R \sim t^{1/2}$$

$$\text{hole area } A \sim R^2 \sim t$$

$$\text{uncoverage } \theta \sim t^2$$

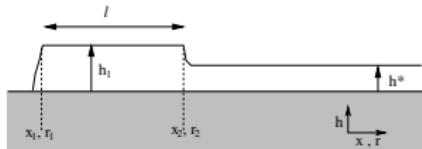
Burhanudin et al Surf. Sci 2006



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Facetted rim



Diffusion-limited dynamics

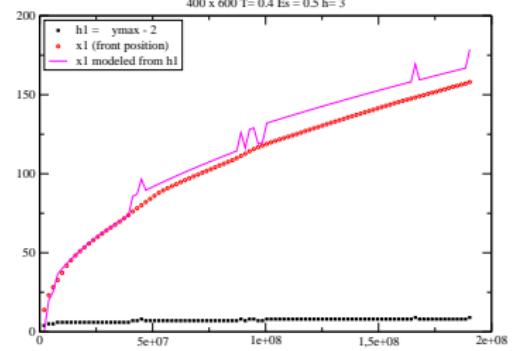
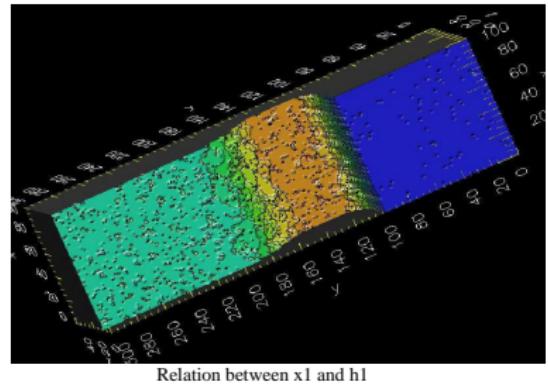
two fronts: $x_1(y, t)$, and $x_2(y, t)$
rim height h_1

$$\begin{aligned} h_1 v_{n1} &= -a^2 D \mathbf{n} \cdot \nabla c|_1 + (x_2 - x_1) \partial_t h_1 \\ (h_1 - h) v_{n2} &= -a^2 D \mathbf{n} \cdot \nabla c|_2 \\ D \Delta c &= 0 \end{aligned}$$

$$c_1 = c_{eq} e^{E_S / Th_1}, \quad c_2 = c_{eq}$$

Straight front

$$\begin{aligned} \sigma &= e^{E_S / Th_1} - 1 \\ H_1 &= (h^{-1} - h_1^{-1})^{-1} \\ x_1 &= \frac{C}{h} + (2a^2 D c_{eq})^{1/2} H_1 \left(\int_{t_0}^t dt' H'_1 \sigma' \right)^{1/2} \end{aligned}$$



Layer-by-layer thickening of the rim

Nucleation + Zipping process

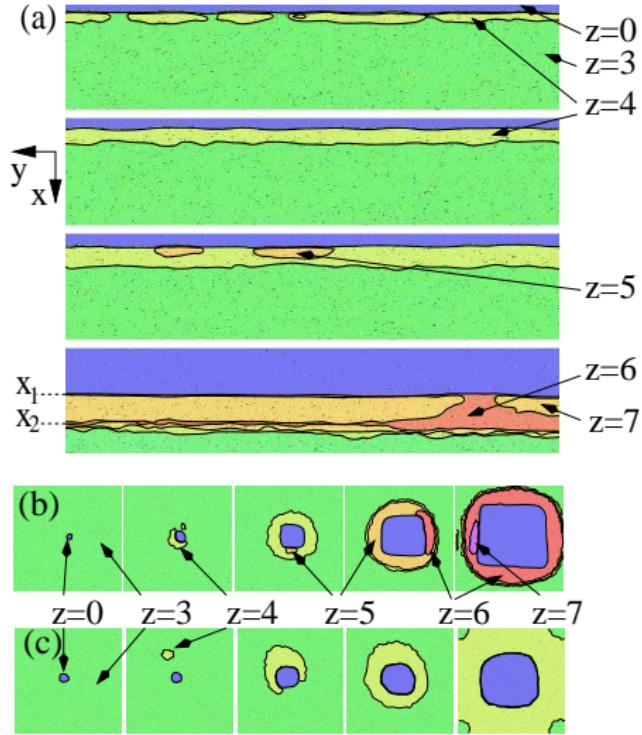
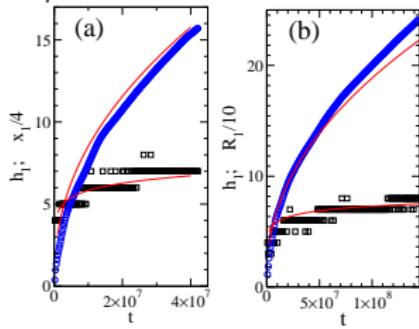
$$\partial_t h_1 = (V_{zip} \mathcal{J})^{1/2}$$

$$\mathcal{J} = \ell \frac{Dc_{eq}}{a^2} \frac{E_S^{3/2} T^{1/2}}{\pi \gamma^2 a^2 h_1^{3/2}} e^{-\pi \gamma^2 a^2 h_1 / TE_S}$$

$$V_{zip} \sim a^2 Dc_{eq} \kappa \left(\frac{E_S}{Th_1} - \frac{a^2 \gamma \kappa}{T} \right)$$

$$V_{zip} \approx C_{zip} a^2 Dc_{eq} \frac{E_S^2}{a^2 Th_1^2 \gamma}$$

C_{zip} unknown number



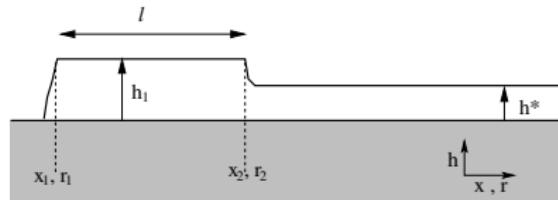
Facetted rim dynamics

Surface diffusion on top facet:

$$\begin{aligned}\Delta\mu &= \frac{E_S}{h_1} \\ \partial_t x_1 &\sim \frac{\Delta\mu}{\ell} \\ \ell(h_1 - h^*) &= x_1 h^* \\ \Rightarrow x_1 &\sim t^{1/2} h_1^{-1/2}\end{aligned}$$

We recover the previous law:

$$\ell \sim h_1 \Rightarrow h_1 \sim x_1^2 \Rightarrow x_1 \sim t^{2/5}$$



Facetted rim

$$\begin{aligned}\partial_t h_1 &\sim e^{-G_c} \sim e^{-\Omega\pi\gamma_{step}^2 h_1/E_S} \\ \Rightarrow h_1 &\sim \ln t \\ \Rightarrow x_1 &\sim t^{1/2} (\ln t)^{-1/2}\end{aligned}$$

Asymptotics

Facetted rim

$$\begin{aligned}x_1(t) &\sim t^{1/2}(\ln t)^{-1/2} \\h_1 &\sim \ln t \\ \ell &\sim t^{1/2}(\ln t)^{-3/2}\end{aligned}$$

Recall continuum model

$$\begin{aligned}x_0(t) &\sim t^{2/5} \\R &\sim t^{1/5}\end{aligned}$$

Distinguish $\ln t$ from $t^{1/5}??$

Si/SiO₂ Leroy et al $x \sim t^{1/3}$

Metal GH Kim et al $x \sim t^{2/5}$.

Instability of a faceted rim: Linear Coarsening

Lin. stab. anal. - **non-steady-state**:

$$x_1(t, y) = x_1(t) + x_1^{(1)}(t, q)$$

$$x_2(t, y) = x_2(t) + x_2^{(1)}(t, q)$$

x_1 unstable, x_2 stable

limit $q\ell \gg 1$

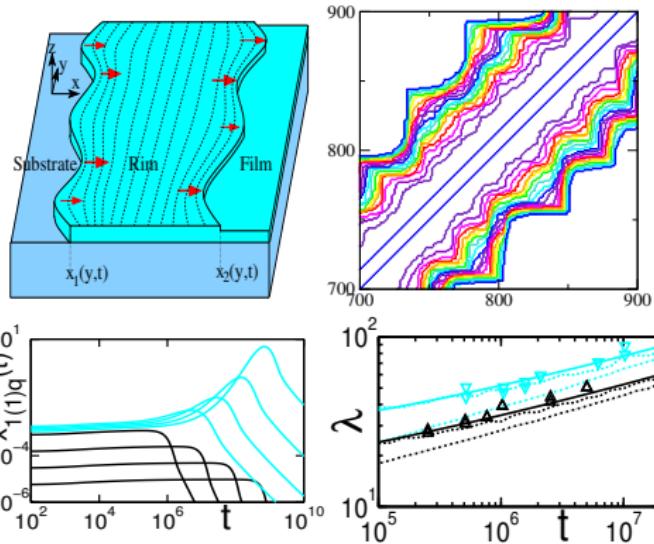
$$x_1^{(1)}(t, q) \sim \exp[a(t)q - b(t)q^3]$$

$$x_2^{(1)}(t, q) \sim \exp[-a(t)q - b(t)q^3]$$

Mode of largest amplitude

$$\lambda_{max} \approx 2\pi \left(\frac{3 \int_0^t dt' \tilde{\gamma}_1 h_{1(0)}^{-1}(t')}{\int_0^t dt' E_S h_{1(0)}^{-2}(t') \ell_{(0)}^{-1}(t')} \right)^{1/2}.$$

- (110) -rough orientation $\tilde{\gamma}_1 \approx \gamma$ constant
Coarsening: $\lambda \sim t^{1/4} (\ln t)^{-1/2}$
Numerical power-law fit $\lambda \sim t^{0.2}$



Instability of a faceted rim: Linear Coarsening

Lin. stab. anal. - **non-steady-state**:

$$x_1(t, y) = x_1(t) + x_1^{(1)}(t, q)$$

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$$x_1^{(1)}(t, q) \sim \exp[a(t)q - b(t)q^3]$$

$$x_2^{(1)}(t, q) \sim \exp[-a(t)q - b(t)q^3]$$

Mode of largest amplitude

$$\lambda_{max} \approx 2\pi \left(\frac{3 \int_0^t dt' \tilde{\gamma}_1 h_{1(0)}^{-1}(t')}{\int_0^t dt' E_S h_{1(0)}^{-2}(t') \ell_{(0)}^{-1}(t')} \right)^{1/2}.$$

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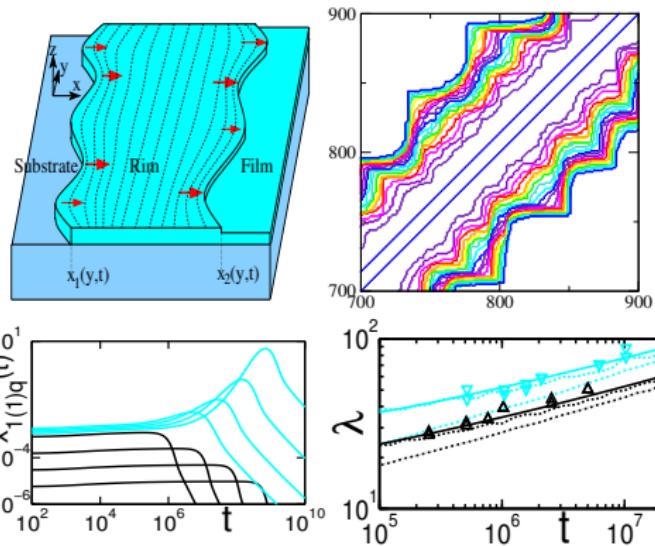
Coarsening: $\lambda \sim t^{1/4} (\ln t)^{-1/2}$

Numerical power-law fit $\lambda \sim t^{0.2}$

- (100) -vertical (100) facet

$$\tilde{\gamma}_1 = Ta/\beta^2 \approx (T/2a)e^{\gamma h_1/T}/h_1$$

Stable

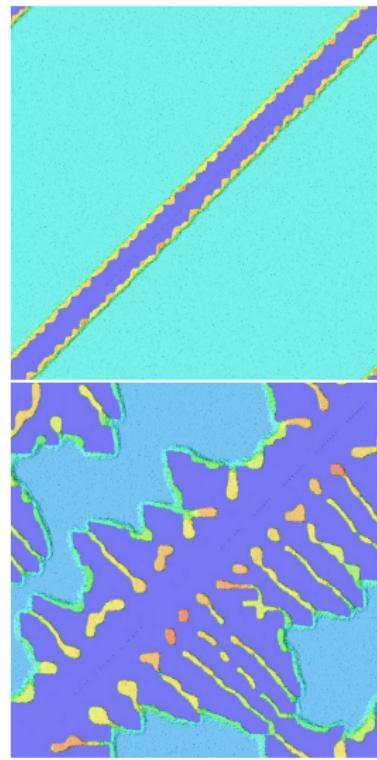


Rim Breakup

KMC

$$t_B \sim E_S^{-2.8} h^{4.2}, \quad \lambda_B \sim E_S^{-1.0} h^{1.2}.$$

Conjecture: λ_B si the finger width?



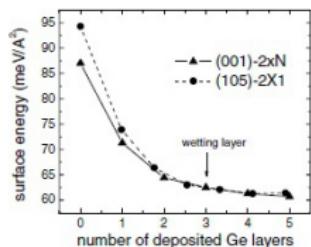
Wetting and dewetting of liquid and solid films

- 1 Static Wetting of liquids and Solids
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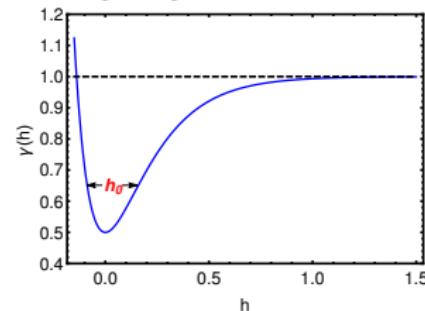
Wetting potential

- Short range electronic effects

Wetting potential Ge/Si G.-H. Lu and F. Liu, PRL, 94 176103 (2005)



Short range repulsive
+ Long range attractive



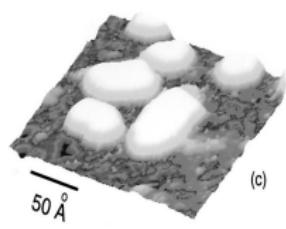
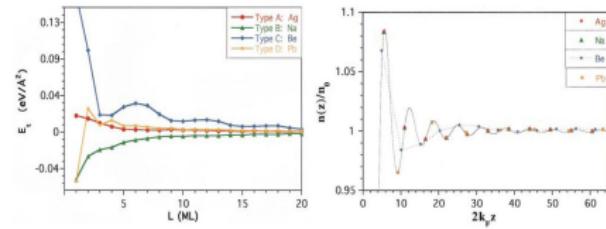
- Van der Waals interactions

$$W_{vdW}(h) = -A/(12\pi h^2)$$

Hamaker constant $|A| \sim 10^{-19} \text{ J}$
attraction/repulsion

- Electronic confinement in metals \rightarrow Magic thickness

Z. Zhang et al, Phys.Rev.Lett.1998,1999



Wetting potential

Credits

- Liquids
see Quéré, Brochard, De Gennes book, or Safran book
- Wetting potential stabilizing wetting film for various instabilities
Golovin et al PRB 2004, Levine et al PRB 2007, Aqua et al PRB 2007
- Hole formation with anisotropy
Khennen PRB 2008
- Nano-island Ostwald ripening
L. Golubovic et al PRE 2013

Question: Consequences of wetting potential on wetting/dewetting dynamics?

Lignes directrices

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Continuum model with Wetting potential

Substrate at $h = 0$

Free energy per unit area :

$$\gamma(h) = \gamma_\infty + \mathcal{W}(h)$$

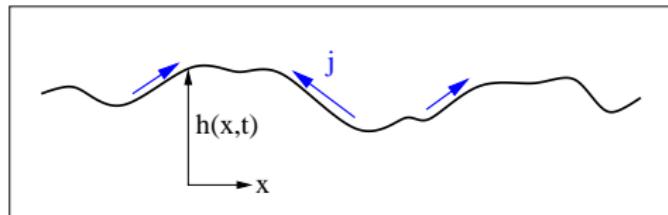
Wetting potential $\mathcal{W}(h) \rightarrow 0$ as $h \rightarrow \infty$

$$\begin{aligned}\mu(x) &= -\gamma_\infty \partial_{xx} h + \gamma'(h) \\ \mathbf{j} &= -\mathcal{M}(h) \nabla \mu \\ \partial_t h &= -\nabla \cdot \mathbf{j}\end{aligned}$$

Far from the substrate: $h \rightarrow \infty$

$$\mathcal{M}(h) \rightarrow \mathcal{M}_\infty$$

$$\gamma(h) \rightarrow \gamma_\infty$$



Lignes directrices

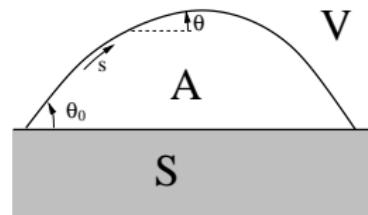
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Non-equilibrium boundary condition

Equilibrium condition at Triple Line

Young-Dupré

$$\gamma \cos \theta_{eq} + \gamma_{int} = \gamma_{sub}$$



Liquids

P.G. de Gennes

Grain Boundaries

U. Czubayko et al, Acta Mater. (1998); M. Upmanyu et al Acta Mater. (2002).

Solid-state wetting

Wang, Jiang, Bao, Srolovitz (2015)

$$v = K(\cos \theta - \cos \theta_{eq})$$

Microscopic origin of the kinetic coefficients:

- Wetting potential?
- Microscopic Kinetic coefficients affected by the vicinity of substrate?

Is this the correction triple line BC?

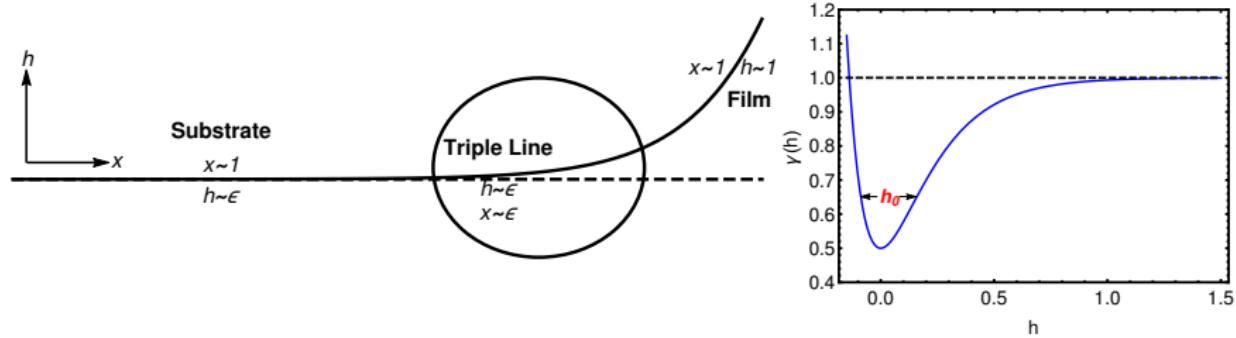
Derive K from mesoscopic model?

Matched asymptotic Expansion

- Expand in small parameter $\epsilon \sim h_0$

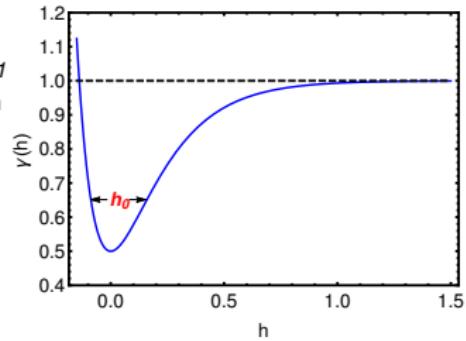
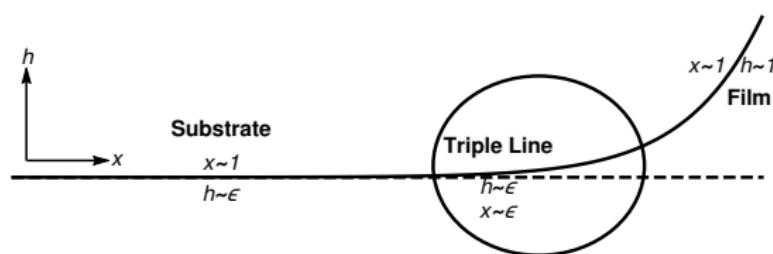
Matched asymptotic Expansion

- Expand in small parameter $\epsilon \sim h_0$



Matched asymptotic Expansion

- Expand in small parameter $\epsilon \sim h_0$



-

$$(a) \text{ Film region} \begin{cases} h \sim O(1) \\ x \sim O(1) \end{cases}$$

$$(b) \text{ TL region} \begin{cases} h = \epsilon H(X, t) \\ x = x_{TL} + \epsilon X \end{cases}$$

$$(c) \text{ Substrate region} \begin{cases} h(x, t) = \epsilon \mathcal{H}(x, t) \\ x = x \end{cases}$$

Kinetic Boundary Conditions

To 0th order, Young & no-flux

$$\theta = \theta_{eq} \quad \frac{\gamma_\infty}{2} \theta_{eq}^2 = \gamma_\infty - \gamma_{min} \quad J = 0$$

... To 3rd order, KBC (Linear / Onsager)

$$\begin{bmatrix} \mathcal{L}_{2v} & \mathcal{L}_{1v} \\ \mathcal{L}_{1v} & \mathcal{L}_{1J} \end{bmatrix} \begin{bmatrix} v \\ J \end{bmatrix} = \begin{bmatrix} [U] \\ -[\mu] \end{bmatrix} \approx \begin{bmatrix} \gamma_\infty(\cos\theta - \cos\theta_{eq}) \\ -\gamma_\infty\kappa + h_{sub}\gamma''_{min} \end{bmatrix}$$

Kinetic Boundary Conditions

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- Thermodynamic Fluxes :
 - v : velocity of triple line
 - J : mass flux through triple line

Kinetic Boundary Conditions

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- Local Thermodynamic Potentials :

$$\begin{aligned} U &= -\frac{\gamma_\infty}{2} (\partial_x h)^2 + \gamma(h). \\ \mu &= -\gamma_\infty \partial_{xx} h + \gamma'(h), \end{aligned}$$

- Thermodynamic Fluxes :

v : velocity of triple line
 J : mass flux through triple line

Kinetic Coefficients

$$\begin{bmatrix} \mathcal{L}_{2v} & \mathcal{L}_{1v} \\ \mathcal{L}_{1v} & \mathcal{L}_{1J} \end{bmatrix} \begin{bmatrix} v \\ J \end{bmatrix} = \begin{bmatrix} [U] \\ -[\mu] \end{bmatrix}$$

Kinetic coefficients

$$\mathcal{L}_{1J} = \int_{-\infty}^{\infty} dX \left(\frac{1}{M(H_0)} - \frac{\Theta(X)}{M(\infty)} - \frac{\Theta(-X)}{M(0)} \right) \sim \frac{\epsilon}{M}$$

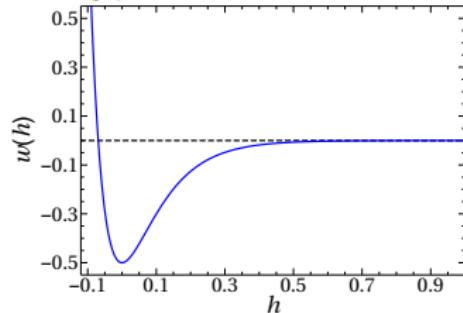
$$\mathcal{L}_{1v} = \int_{-\infty}^{\infty} dX \left(\frac{H_0}{M(H_0)} - \Theta(X) \frac{X \partial_x h_0(x_{TL})}{M(\infty)} \right) \sim \frac{\epsilon^2}{M}$$

$$\mathcal{L}_{2v} = \int_{-\infty}^{\infty} dX \left[\frac{H_0^2}{M(H_0)} - \frac{\Theta(X)}{M(\infty)} (X \partial_x h_0(x_{TL}))^2 \right] \sim \frac{\epsilon^3}{M}$$

In most cases $\theta \sim \theta_{eq}$?

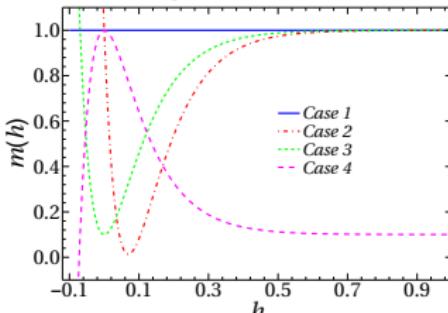
Numerical simulations

Wetting potential

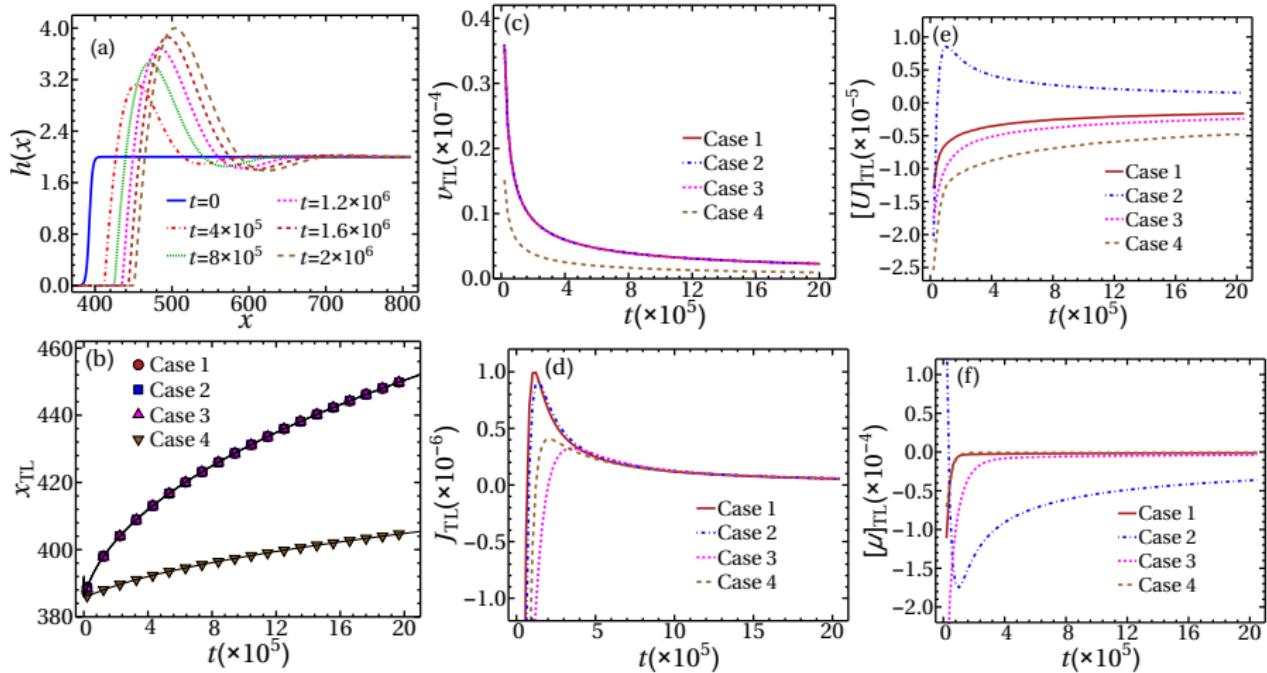


Mobility

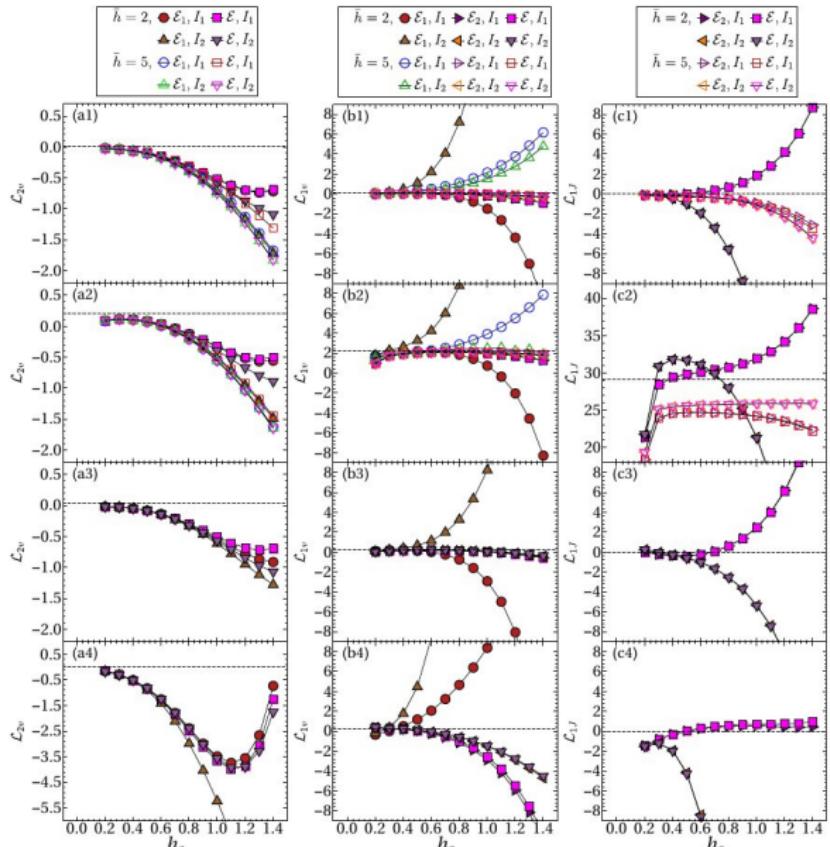
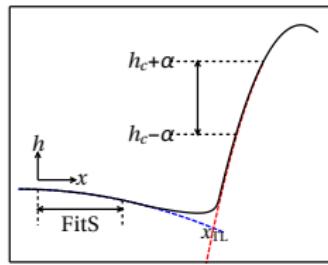
- case 1 constant mobility
- case 2 reduced mobility in the triple line region
- case 3 asymmetric: lower mobility in the substrate
- case4 asymmetric: lower mobility in the film



Numerical simulations



Numerical simulations

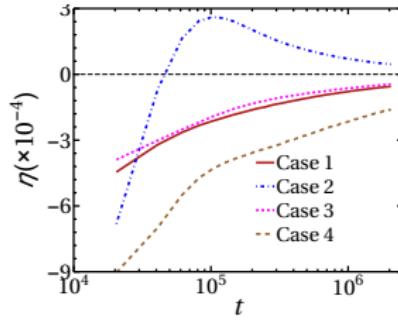
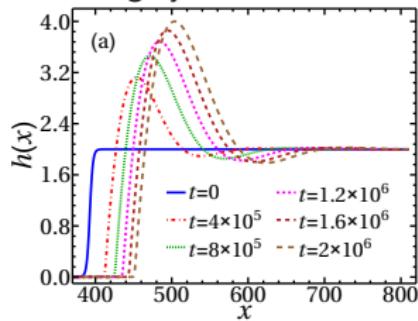


Numerical simulations

Dynamic contact angle θ_D

$$\eta = \frac{\theta_{eq} - \theta_D}{\theta_{eq}}$$

Dewetting dynamics



Summary on Kinetic Boundary Condition

- 2 Kinetic Boundary Conditions for v and J
- Numerical validation
- Convergence of kinetic coefficients.
 $W(h) - W(\infty) \sim h^{-n}$, with $n > 3$
 $M(h) - M(\infty) \sim h^{-m}$, with $m > 3$
Van der Waals $n = 2$??

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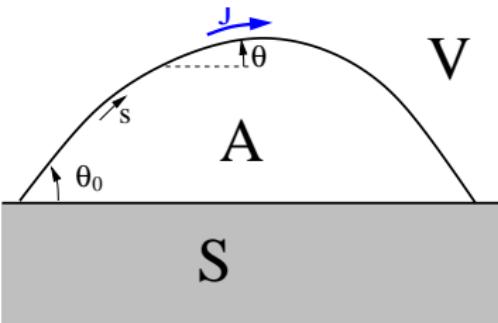
Surface Diffusion Mullins' Model

Mullins model $\mu = \Omega \tilde{\gamma} \kappa$

$$\begin{aligned} j &= -\frac{Dc}{k_B T} \partial_s \mu \\ v_n &= -\Omega \partial_s j \end{aligned}$$

$$v_n \sim \partial_{ss} \kappa$$

Equil. contact angle $\theta = \theta_0$



Dewetting dynamics

Wong, Voorhees, Miskis, Davis, Acta Mater. 2000

Brandon and Bradshaw

Small slopes $\theta \ll 1$

$$\lambda \sim \theta R, \text{ and } h \sim \theta^2 R$$

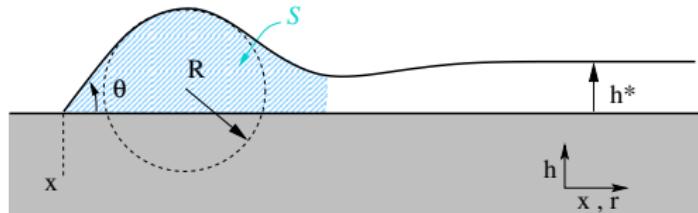
$$\partial_t x = \theta^{-1} v_n \sim \theta^{-1} \partial_{ss} \kappa \sim \theta^{-1} \lambda^{-2} R^{-1}$$

$$S \sim h \lambda \sim R^2 \theta^3$$

$$\partial_t S = v \bar{h}$$

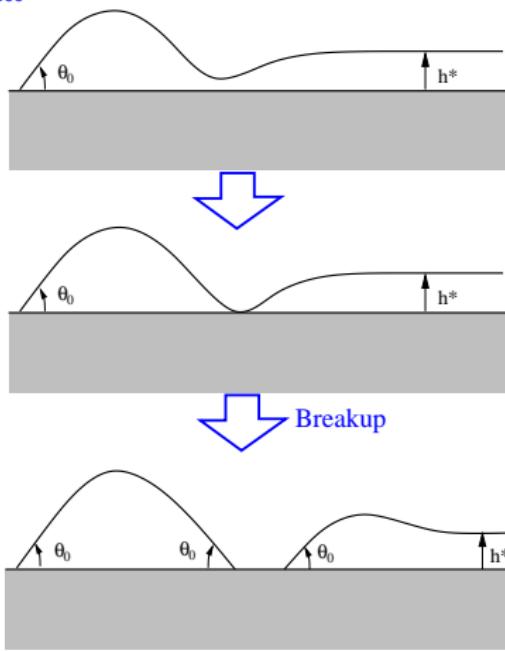
$$h \sim \theta^{4/5} \bar{h}^{1/5} t^{1/5}$$

$$x \sim \theta^{3/5} \bar{h}^{-3/5} t^{2/5}$$



Mass shedding

Wong, Voorhees, Miskis, Davis, Acta Mater. 2000



Scaling solution $\bar{h} \sim \theta^{4/5} \bar{h}^{1/5} T^{1/5}$

$$T_c^{WV} = a \frac{\bar{h}^4}{\theta_0^4}; \quad a \approx 2 \times 10^5.$$

Wong, Voorhees, Miskis, Davis, Acta Mater. 2000

Oliver Pierre-Louis (ILM-Lyon, France.)

Wetting and dewetting of solid films

Numerical Simulation

Wetting Potential

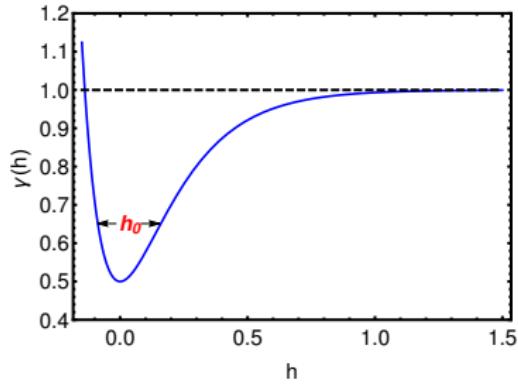
$$\gamma(h) = \gamma_\infty + \mathcal{W}(h)$$

$$\mathcal{W}(h) = (\gamma_\infty - \gamma_{min})(e^{-h/h_0} - 2e^{-h/2h_0})$$

$$h_{min} = 0; \quad \gamma(h_{min}) = \gamma_{min}.$$

Young Contact angle:

$$\gamma_\infty \cos(\theta_0) = \gamma_{min}$$

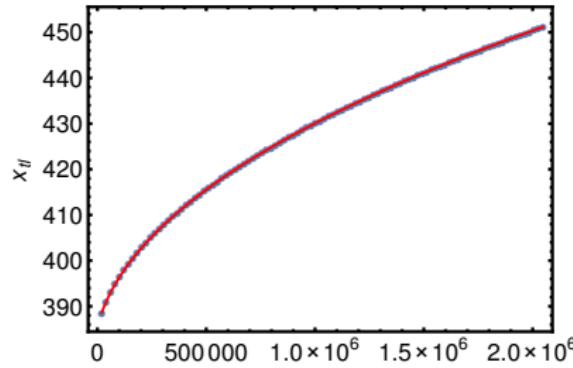
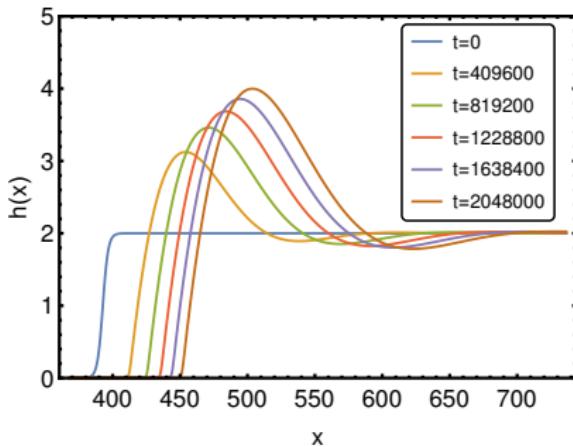


Film profile

Dewetting from film edge
 $\theta_0 = 10^\circ$ and $h_0 = 0.05$

Quantitative agreement with Wong-Voorhees

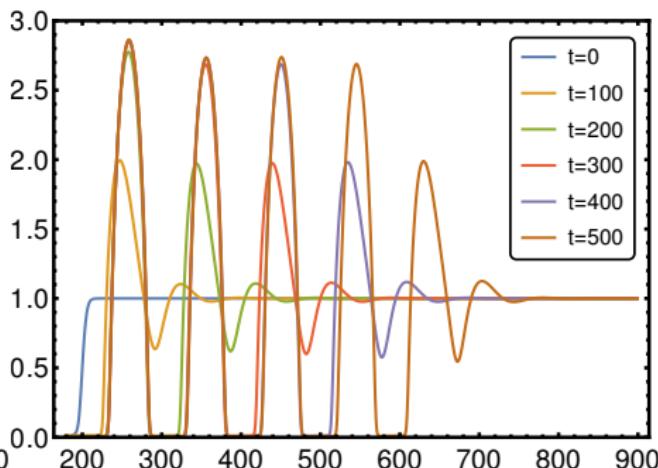
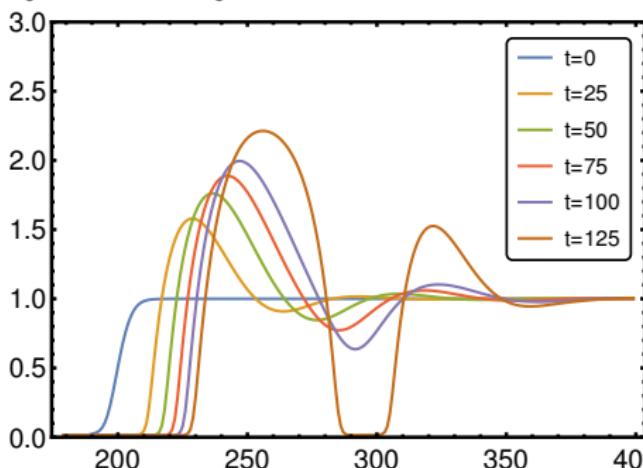
$$x_{tl}(t) = x_0 + at^{1/5} + bt^{2/5}$$



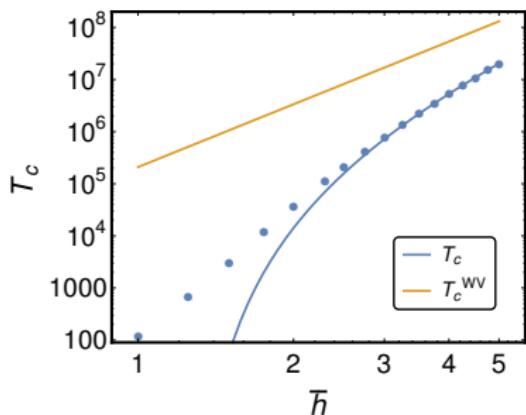
Mass Shedding

Periodic Mass shedding

$$\theta_0 = 60^\circ \text{ and } h_0 = 0.1$$



Accelerated Mass shedding



- without wetting potential:
Wong and Voorhees solution $\bar{h} \sim \theta^{4/5} \bar{h}^{1/5} T^{1/5}$
- $$T_c^{WV} = a \frac{\bar{h}^4}{\theta_0^4}; \quad a \approx 2 \times 10^5.$$
- with wetting potential $\mathcal{W}(h)$:
Mass shedding accelerated by orders of magnitude

Cutoff height h_{cut} within WV solution: $\bar{h} - h_{cut} \sim \theta^{4/5} \bar{h}^{1/5} T^{1/5}$

$$T_c = A_1 \frac{(\bar{h} - h_{cut})^5}{\theta_0^4 \bar{h}}$$

With $A_1 = 1.5 \times 10^5$, and $h_{cut} = 1.2$

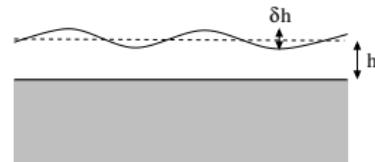
Small thicknesses: spinodal dewetting

Linear stability analysis : $h = \bar{h} + \delta h$

$$\delta h \sim e^{i\omega t + iqx}$$

$$i\omega = \mathcal{M}(\bar{h}) q^2 [-\gamma_\infty q^2 + W''(\bar{h})]$$

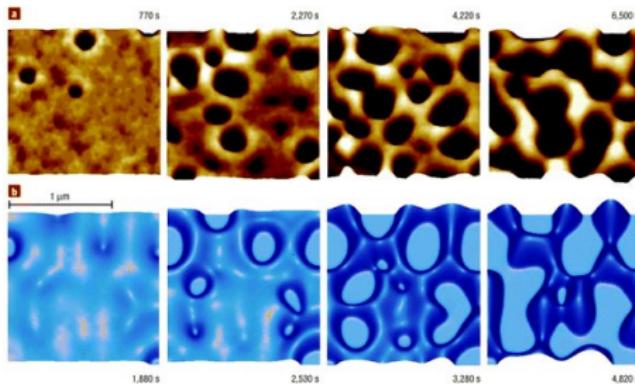
Spinodal Instability if $W''(\bar{h}) \leq 0$



$$\lambda_{LS} = \frac{2^{3/2}\pi\bar{\gamma}^{1/2}}{W''(\bar{h})^{1/2}}$$

$$T_{LS} = \frac{4\bar{\gamma}}{\mathcal{M} W''(\bar{h})^2}$$

Liquids



Embedded Animation

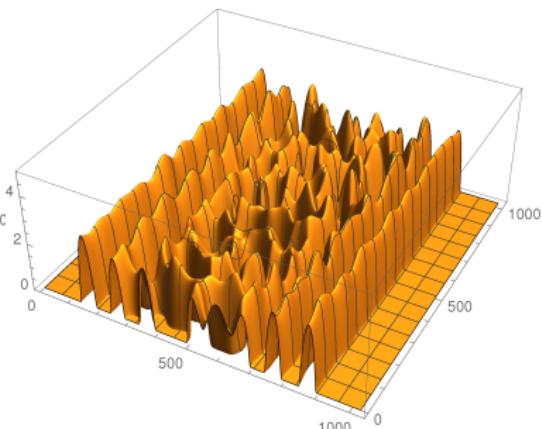
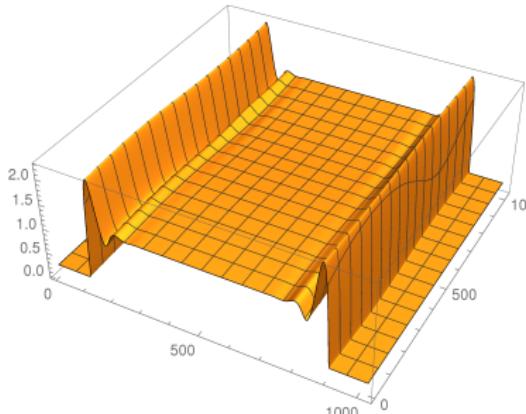
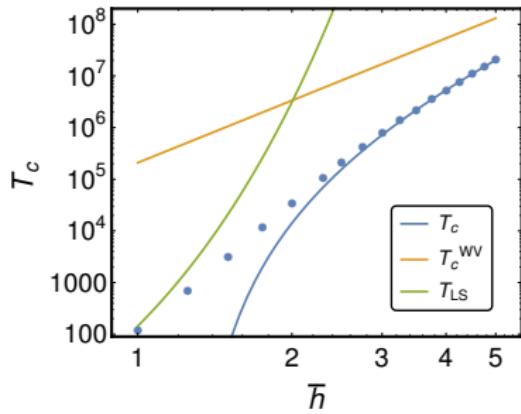
Ashwani Tripathi, ILM-Lyon

Small thicknesses: spinodal dewetting

Linear stability analysis : $h = \bar{h} + \delta h$

Spinodal Instability if $W''(\bar{h}) \leq 0$

$$T_{LS} = \frac{4\bar{\gamma}}{\mathcal{M}W''(\bar{h})^2}$$



Accelerated mass shedding

Ashwani Tripathi, ILM-Lyon

Lignes directrices

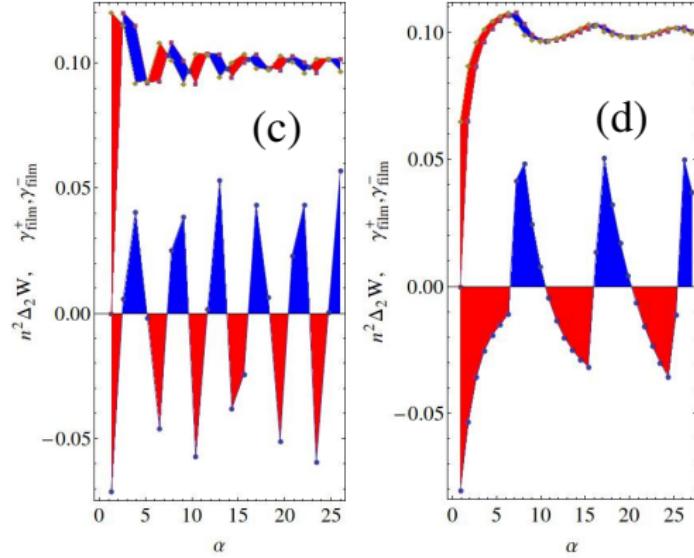
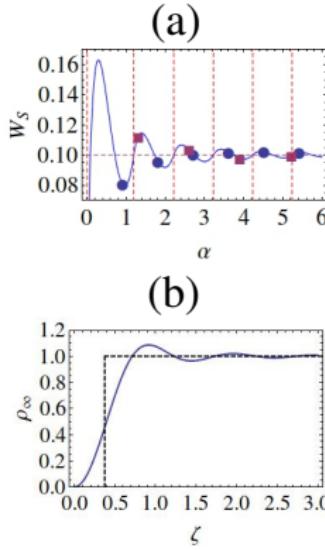
- 1 Static Wetting of liquids and Solids
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Electronic Quantum confinement

Free electron model

$$W_{EC}(h) \approx -\frac{E_{fb}}{(h+2b)^2} \frac{\pi}{36\sqrt{3}} \cos(2k_{fb}h)$$

E_{fb} , k_{fb} Fermi energy and wavevect,
 $b = 3\pi k_{fb}/8$

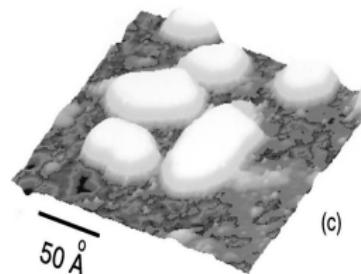
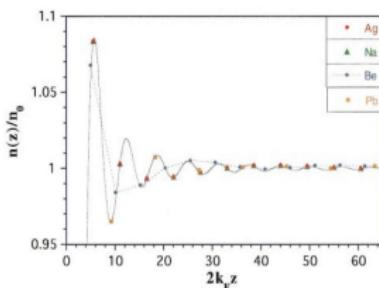
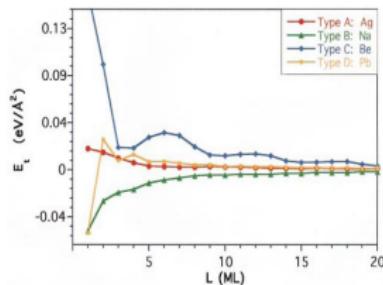


(a) Al(111) (purple squares), Ag(111) (blue circles)
(c) Al(111) ,(d) Ag(111) blue-Stable, red-Unstable

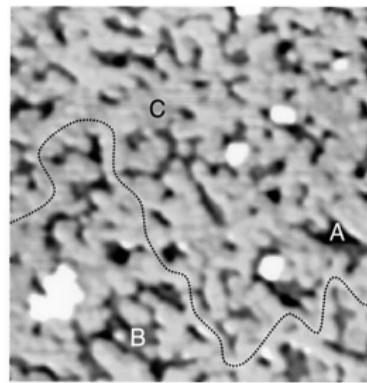
Magic heights and labyrinthine patterns

Metals/ semicon or insulator: Electronic confinement → Magic thickness

Z. Zhang et al., Phys. Rev. Lett. 1998, 1999



Experiments Ag/Si(111)



SOS KMC model with magic height

KMC simulations SOS

$$z \neq 1 \text{ and } z \neq h_*$$

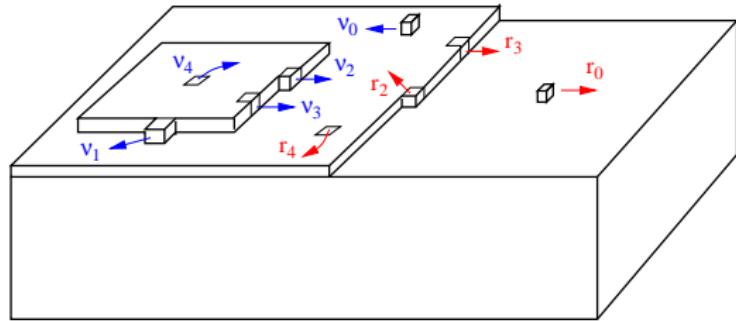
$$z = 1$$

$$z = h_*$$

$$\nu_n = \nu e^{-(nJ + J_0)/T}$$

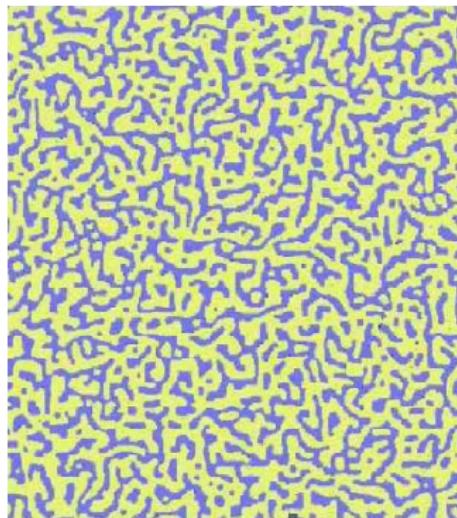
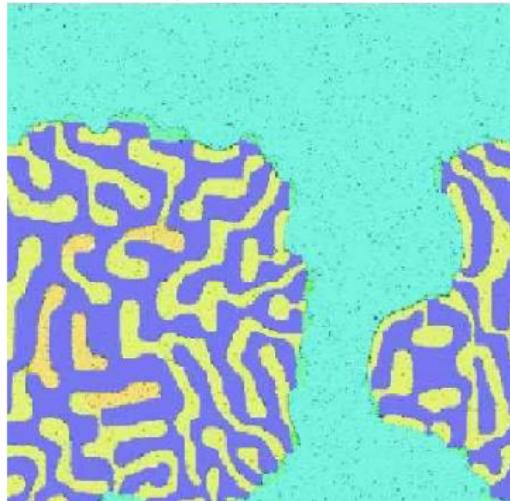
$$r_n = \nu e^{-(nJ + J_0 - E_S)/T}$$

$$r_n^* = \nu e^{-(nJ + J_0 - E_*)/T}$$



KMC simulations with magic height

A. Chame, OPL, Phys Rev B 2014



$\lambda \sim 30\text{nm}$

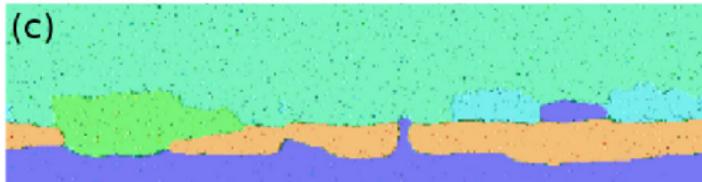
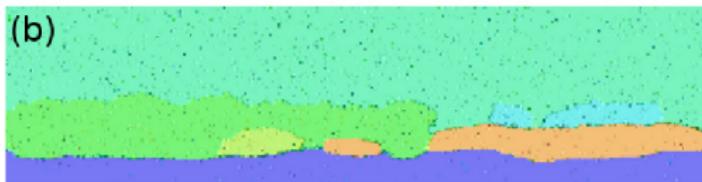
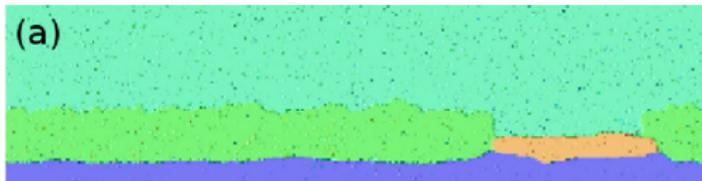
Semi-quantitative agreement with experiments

Magic-height rim

800×800 , $T = 0.4$, $h = 3$, $E_S = 0.4$, $h_* = 7$, $E = -0.5$

Induced nucleation and incomplete closure

A. Chame, OPL, Phys Rev B 2014



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Conclusion

Consequences of the wetting potential:

- Triple line kinetics: 2 Boundary Conditions
A. Tripathi, OPL, preprint 2016
- Attractive part in the wetting potential → accelerated mass shedding
A. Tripathi, OPL, preprint 2016
 - Decreasing thickness: VW, cutoff height, Linear spinodal instability
- Quantum Magic height → rim breakup and labyrinthine patterns
A. Chame, OPL, Phys Rev B 2014
 - Incomplete rim closure
 - Induced hole nucleation behind the rim

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P. Gaillard, ILM, Lyon, France

M. Ignacio, ILM, Lyon, France

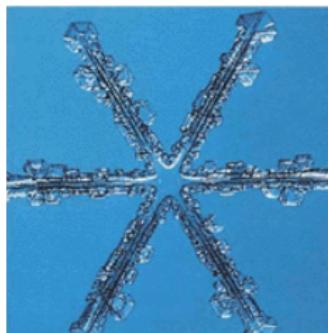
Wetting and dewetting of liquid and solid films

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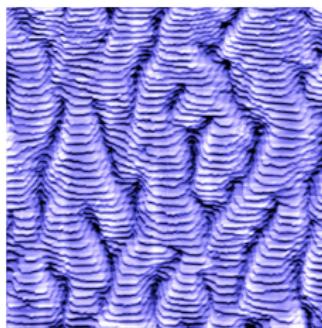
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Growth shapes



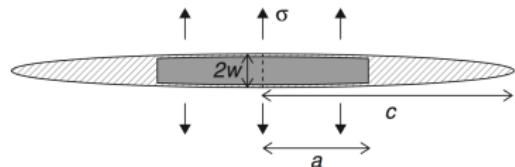
Snowflake Yoshi Furukawa, Hokkaido, Japan



Growth Cu(1,1,17) Maroutian, Ernst, Saclay, France

Force of crystallization and rims

Weathering, aging of building material e.g. cements

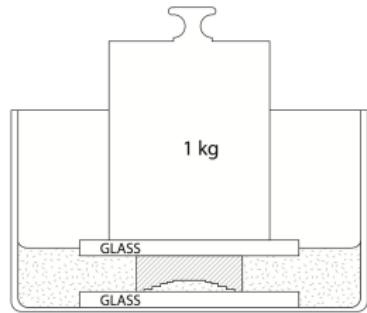


A. Ryne, P. Meakin, A. Malthe-Sørensen, B. Jamtveit and D. K. Dysthe EPL
96 (2011)



Espinoza-Marzal et al Accounts of Chem. Res. (2009)

Force of crystallization and rims



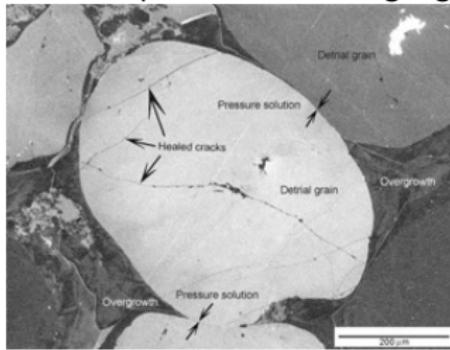
becker and Day, 1916



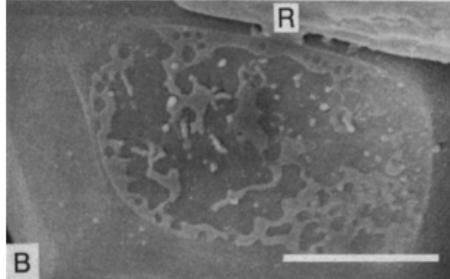
A. Røyne PhD Thesis UiO

Pressure solution

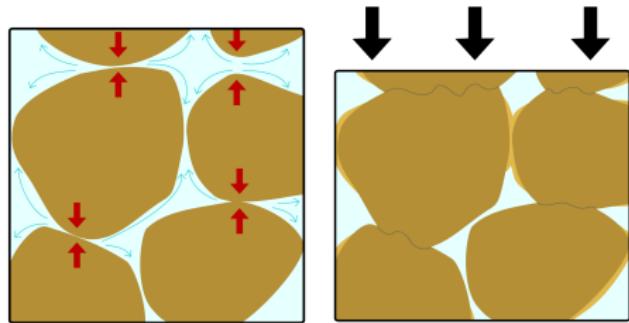
Rock compaction, weathering, aging of building material e.g. cements



Univ. Bern <http://www.geo.unibe.ch/>



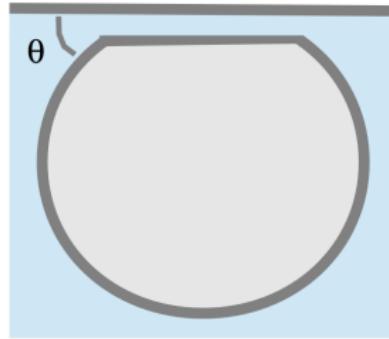
Quartz aggregates at high temperatures S.F. Cox and M.S. Paterson



Equilibrium Wetting state

Equilibrium of an immersed solid in a liquid \sim Wetting

Equilibrium Contact angle: $\gamma_\infty \cos \theta = \gamma_{min}$

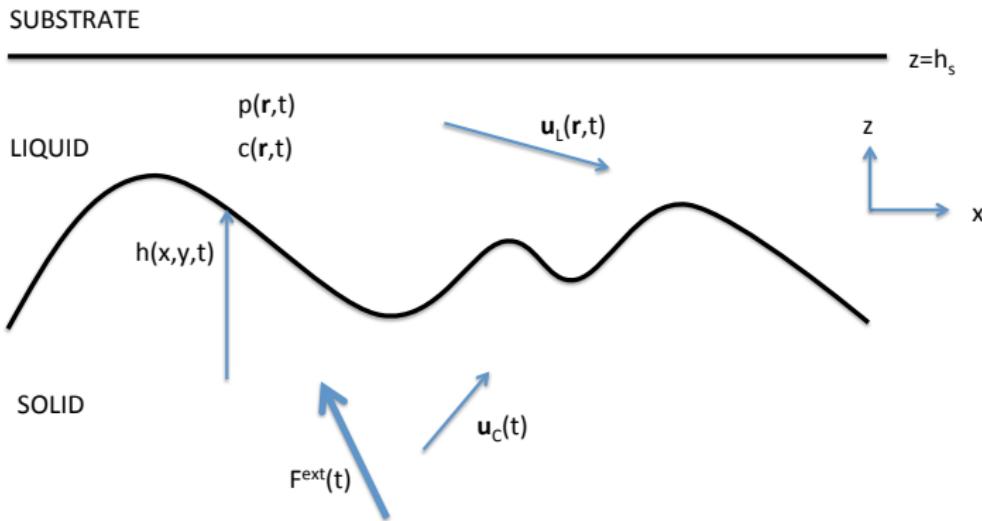


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Strategy

Dynamics at contacts → Thin film approach



Film thickness

$$\zeta(x, y, t) = h_s - h(x, y, t).$$

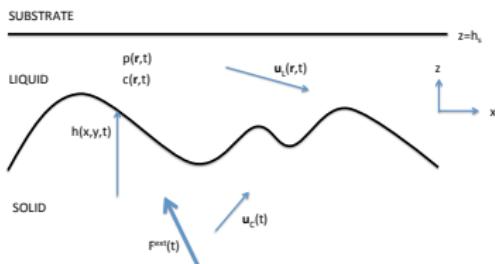
Assumptions

Model ingredients

- Mass transport
 - diffusion in liquid D
 - Hydrodynamics / viscosity η
- Force / energy
 - Force \mathbf{F}_C on a rigid solid
 - surface tension $\gamma(\mathbf{n})$
 - Interaction potential $U(\zeta)$, disjoining pressure $U'(\zeta)$

Basic assumptions

- Small slopes: $|\nabla h| \ll 1$
- Liquid always present $\zeta > 0$
- Rigid solid, no rotation, translation along z

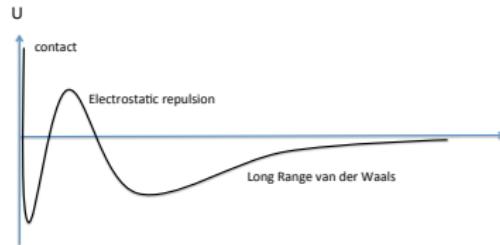


More on interactions

Ingredients in the interaction potential:

- Electrostatic $U(\zeta) \sim \exp[-\zeta/\lambda_D]$
- van der Waals $U(\zeta) \sim -A/\zeta^2$
- Hydration $U(\zeta) \sim \exp[-\zeta/\lambda]$
- liquid ordering, solute effects, etc.

DLVO (electrostatics + van der Waals)



Thin film model

Lubrication limit $|\nabla h| \ll 1$

Global mass conservation

$$\rho_C(\partial_t \zeta + u_{Cz}) = -\rho_L \nabla_{xy} \cdot \left[\frac{\zeta^3}{12\eta} \nabla_{xy} p \right] + \rho_L \partial_t \zeta$$

Conservation of crystal molecules

$$-\frac{\partial_t \zeta + u_{Cz}}{\Omega} + \partial_t [\zeta c_{eq}] - \nabla_{xy} \cdot \left[\frac{\zeta^3}{12\eta} c_{eq} \nabla_{xy} p \right] = \nabla_{xy} \cdot [\zeta D \nabla_{xy} c_{eq}].$$

Local equil. conc. $c_{eq} = c_0 e^{\Delta\mu/k_B T}$ with

$$\frac{\Delta\mu(x, y, t)}{\Omega} = -\tilde{\gamma}_1 \partial_{x_1 x_1} h - \tilde{\gamma}_2 \partial_{x_2 x_2} h - U'(\zeta) + \left(\frac{\rho_C}{\rho_L} - 1 \right) p$$

Force balance

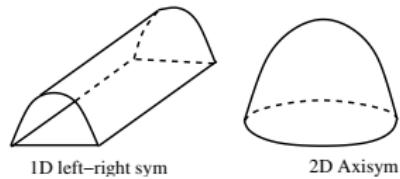
$$F_{Cz} = \iint_{\text{contact}} dA (p - p^{ext} + W'(h))$$

Unknowns: $p(x, y, t)$, $\zeta(x, y, t)$, $u_{Cz}(t)$

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A Simple case



Assumptions

- Geometry: axisymmetric (2D), or ridge $x \rightarrow -x$ (1D)
- Equal densities $\rho_L = \rho_C$
- Dilute limit $\Omega c \ll 1$
- Linear thermodyn $\Delta\mu \ll k_B T$

Evolution equation, axisymmetric case

$$\partial_t \zeta + u_{Cz} = -D_e \frac{1}{r} \partial_r \left[r \zeta \partial_r (\gamma \partial_{rr} \zeta + \frac{\gamma}{r} \partial_r \zeta - U'(\zeta)) \right]$$

$$D_e = \frac{D \Omega^2 c_0}{k_B T}.$$

Force balance

$$u_{Cz} \int_0^R 2\pi r dr \int_r^R dr' \frac{6\eta r'}{\zeta(r')^3} = F_{Cz}^{2D} + 2\pi \int_0^R dr r U'(\zeta)$$

Viscous force

Disjoining force

Steady-states

$$0 = u_{Cz} + D_e \frac{1}{r} \partial_r \left[r\zeta \left(\gamma \partial_{rr}\zeta + \frac{\gamma}{r} \partial_r \zeta - U'(\zeta) \right) \right]$$

Large forces

- flat contact
- small curvature
- negligible surface tension effects
- **Analytical solution**

Steady-states

γ terms negligible in the contact

Repulsive potential

$$U(\zeta) = \frac{A}{\zeta^n}$$

Crystal surface profile

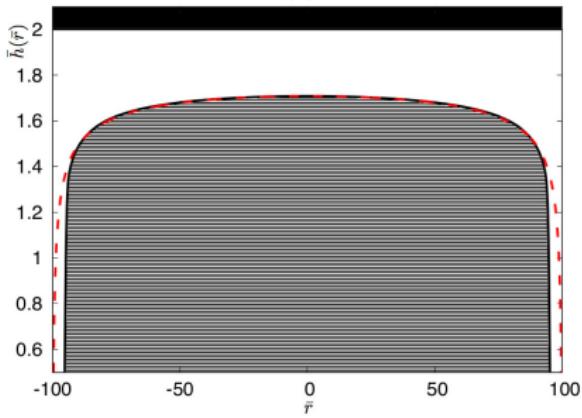
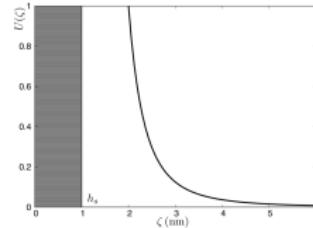
$$\zeta(r) = \left(\frac{\zeta_0^n}{1 - r^2/R^2} \right)^{1/n}.$$

$$R^2 = \frac{4D_e(n+1)A}{\zeta_0^n u_{Cz}}$$

Full numerical solution

$$n = 3$$

BC: fixed c and ζ



Steady-states

Force Balance

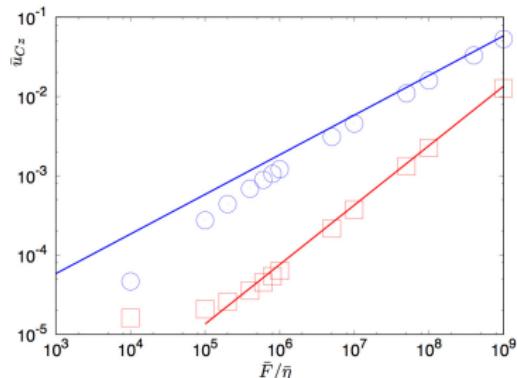
$$\frac{F_{Cz}^{2D}}{\pi R^2} = 12\eta \frac{n^2}{(2n+3)(n+3)} \left(\frac{1}{D_e A(n+1)} \right)^{\frac{3}{n}} \left(\frac{R^2}{4} u_{Cz} \right)^{\frac{n+3}{n}}$$

$$+ \frac{n^2}{2n+1} A^{-\frac{1}{n}} \left(\frac{1}{D_e(n+1)} \right)^{\frac{n+1}{n}} \left(\frac{R^2}{4} u_{Cz} \right)^{\frac{n+1}{n}}$$

Viscous force $\bar{\eta} = 1$

Disjoining force $\bar{\eta} = 10^3$

$$\bar{\eta} = \frac{D_e}{\lambda^2} \eta = \frac{D \Omega^2 c_0}{\lambda^2 k_B T} \eta$$



$$u_{Cz}^{2D} \sim R^{-\frac{4n+2}{n+1}} (F_{Cz}^{2D})^{\frac{n}{n+1}}$$

$$u_{Cz}^{2D} \sim R^{-\frac{4n+6}{n+3}} \left(\frac{F_{Cz}^{2D}}{\eta} \right)^{\frac{n}{n+3}}$$

Steady-states

Power-law repulsive potential

- "flat" profile
- dissolution velocity increases with load (power-law)
- Similar results 1D & 2D axisym

Orders of Magnitude

- Calcite
 - ζ scale \sim nm
 - x scale \sim 10nm
 - t scale \sim 10^{-1} s
 - p scale \sim MPa
 - η scale \sim 10^2 Pa s
- Salts (NaClO_3)
 - ζ scale \sim nm
 - x scale \sim 1 to 10nm
 - t scale \sim 10^{-6} s
 - p scale \sim MPa
 - η scale \sim 10^{-2} Pa s

Steady-states

γ terms neglected in the contact

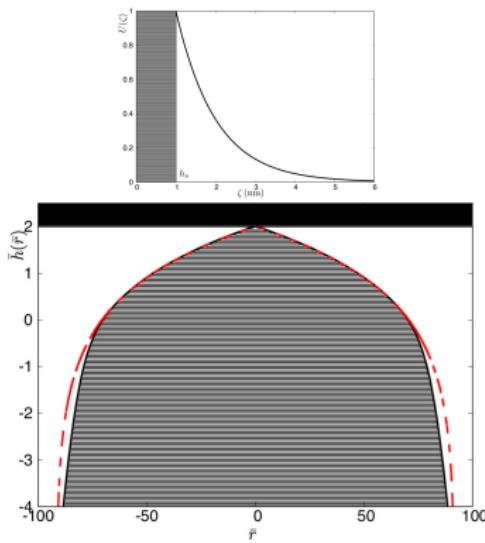
Repulsive potential finite

$$U(\zeta) = Ae^{-\zeta/\lambda}$$

Pointy conical shape

$$\zeta_{sing} \approx 2^{1/2} \frac{\lambda}{R} |r|$$

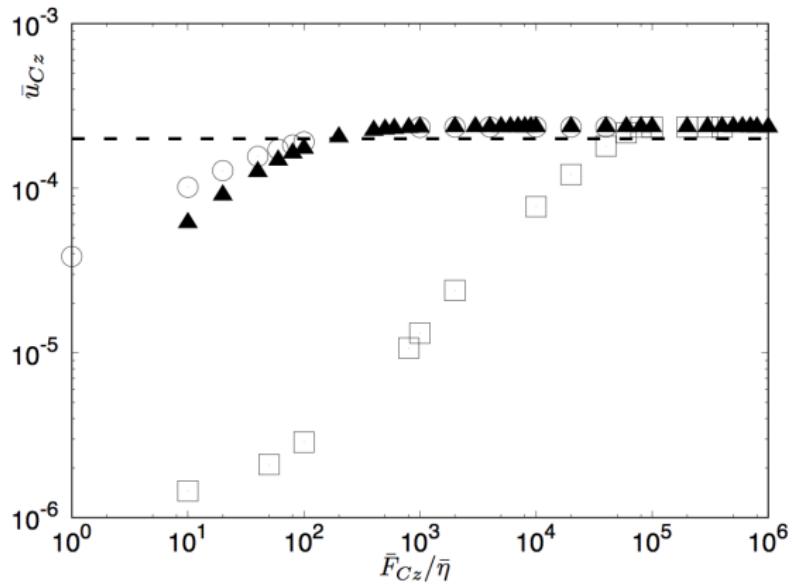
Complete solution: no contact



Steady-states

Constant velocity!

$$u_{Cz}^{2D} = D_e \frac{4A}{R^2}$$



$$\bar{\eta} = 5 \times 10^2, 5 \times 10^{-1}, 5 \times 10^{-4}$$

Steady-states

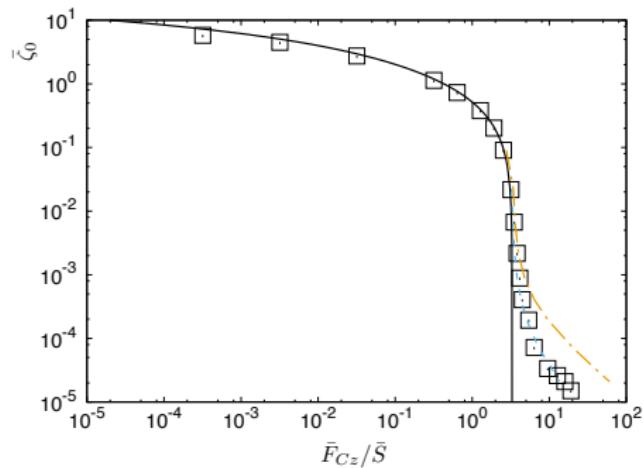
Force Balance

$$\frac{F_{Cz}^{2D}}{\pi R^2} = \left[12\eta D_e \frac{A}{\lambda^3} \psi\left(\frac{\zeta_0}{\lambda}\right) \frac{e^{\frac{\zeta_0}{\lambda}}}{1 + \frac{\zeta_0}{\lambda}} + \frac{A}{4\lambda} \left(\frac{2\zeta_0}{\lambda} + 1 \right) \frac{e^{-\frac{\zeta_0}{\lambda}}}{1 + \frac{\zeta_0}{\lambda}} \right]$$

$\lim_{z \rightarrow 0} \psi(z) = (1 - \ln 2).$

Finite Force four touching contact $\zeta_0 = \zeta(0) = 0$

$$F_c^{2D} = \left[12\eta D_e \frac{A}{\lambda^3} (1 - \ln(2)) + \frac{A}{4\lambda} \right] \pi R^2$$



Origin of deviation at small ζ_0 ?

Steady-states

Line tension effect

$$0 = u_{Cz} + D_e \frac{1}{r} \partial_r \left[r\zeta \left(\gamma \partial_{rr}\zeta + \frac{\gamma}{r} \partial_r \zeta - U'(\zeta) \right) \right]$$

Taylor expand

$$\zeta^{tip} = \zeta_0 + \frac{r^2}{2} \partial_{rr}\zeta_0$$

Diverging viscous contribution

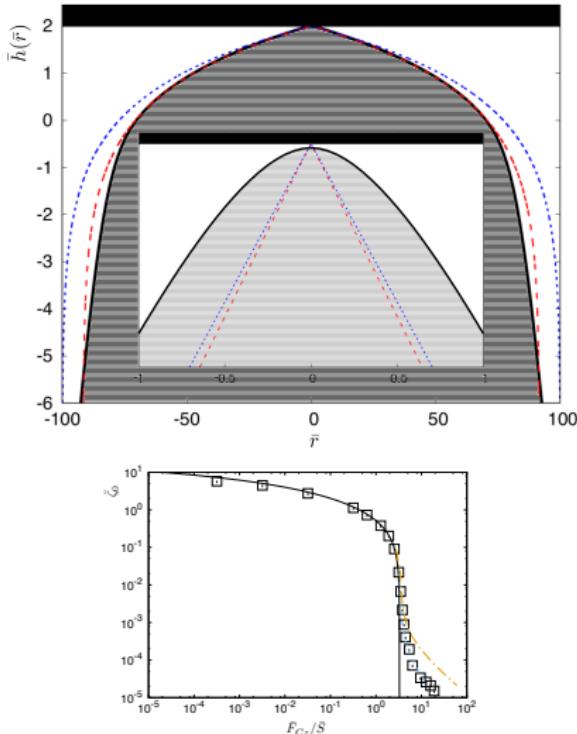
$$F_{tip}^{2D} = \eta \frac{6\pi u_{Cz}}{(\partial_{rr}\zeta_0)^2 \zeta_0}$$

Matched asymptotic analysis:

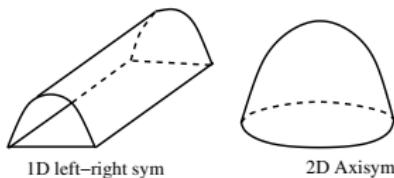
$\partial_{rr}\zeta_0 \rightarrow \text{cst}$ when $\zeta_0 \rightarrow 0$

$$F_{tip}^{2D} = \frac{24\pi\eta\gamma^2 D_e \lambda^2}{C_{2D}^2 A R^2} \frac{1}{\zeta_0}$$

$$C_{2D} \approx 0.015$$

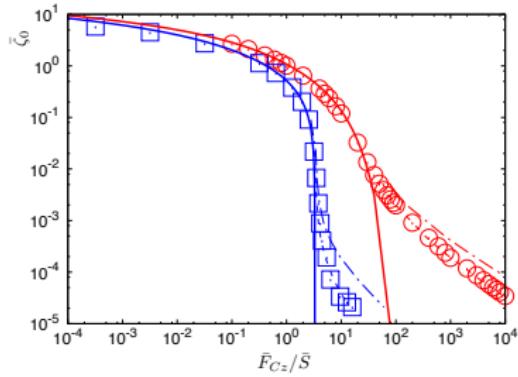


1D vs 2D



- 2D touching contact without γ
- 1D log div. no contact without γ : $F_{Cz} \sim \ln[1/\zeta_0]$

but similar regularization of tip by surface tension



Steady-states

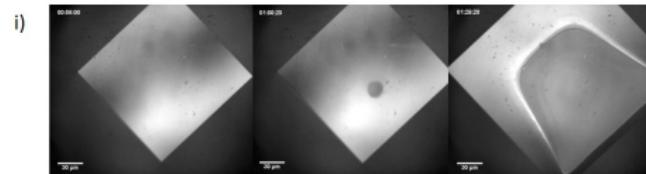
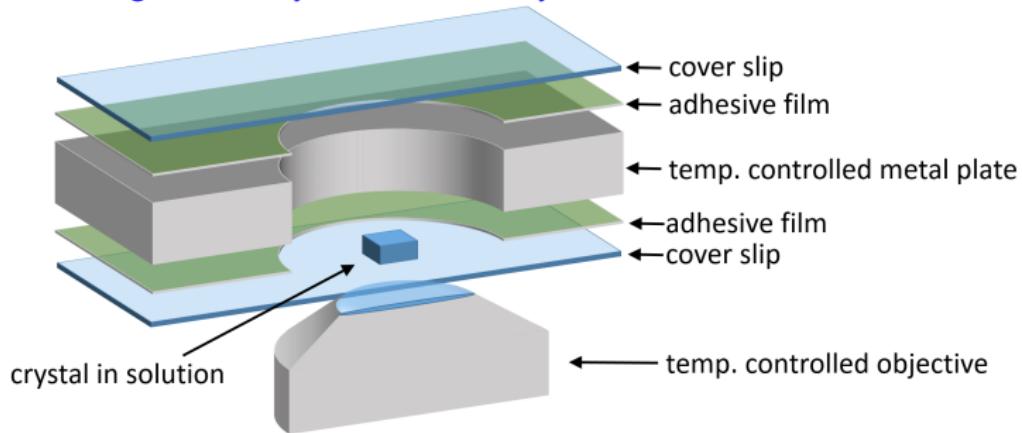
- 2D (touching contact without γ) vs 1D (log div. no contact without γ)
but similar regularization by surface tension
- **Interactions control contact shapes and dissolution rates in pressure solution**
 - flat vs pointy
 - increasing with load vs constant
- Experiments: Need of single-contact measurements (SFA/AFM)
- Rock compaction problem: interaction between contacts

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Experimental setup

Felix Kohler and Dag Kristian Dysthe, UiO, Norway



Model

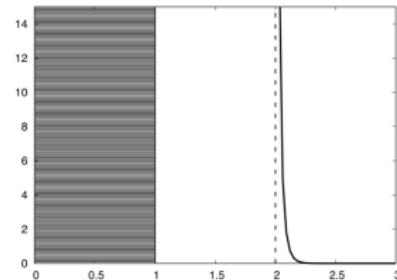
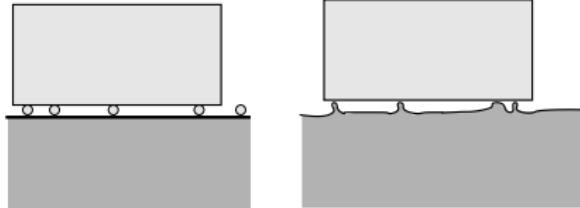
Experiments:

$\zeta \sim 10$ to 100nm

Interaction: Roughness or (nano)particles !

Thin film Model
Potential (Yukawa-like)

$$U(\zeta) = A \frac{e^{\frac{-(\zeta - \zeta_c)}{\lambda \zeta_c}}}{\zeta - \zeta_c},$$



Simulations

Boundary conditions:

- Fixed thickness ζ_b at the boundaries
- Fixed supersaturation at the boundaries

Force: weight

$$F_{Cz} = (\rho_C - \rho_L)gL^3$$

Simulate facet?

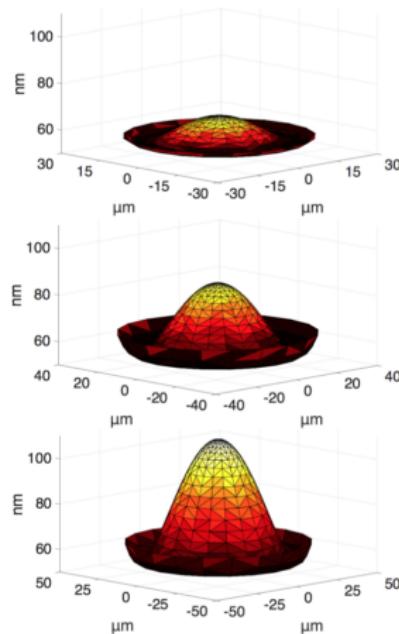
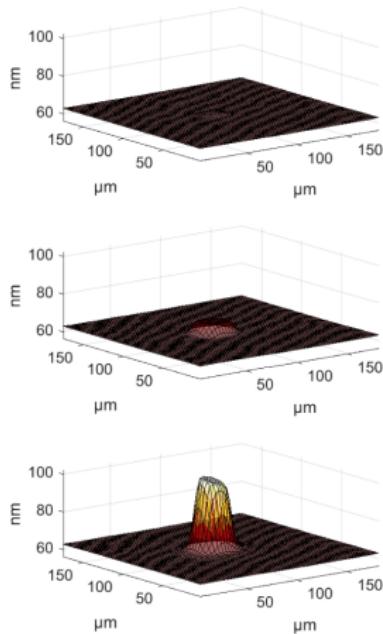
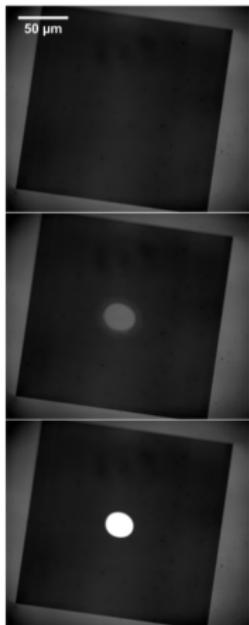
→ diverging stiffness $\tilde{\gamma} = \gamma + \gamma''$

Experiments vs Theory

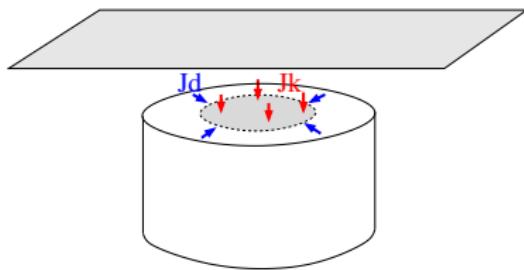
Experiments: growth in fixed supersaturation

Simulation: growth for a contact with a fixed size

Summary of observations



Heuristics



Mass balance / Axisymmetric geometry

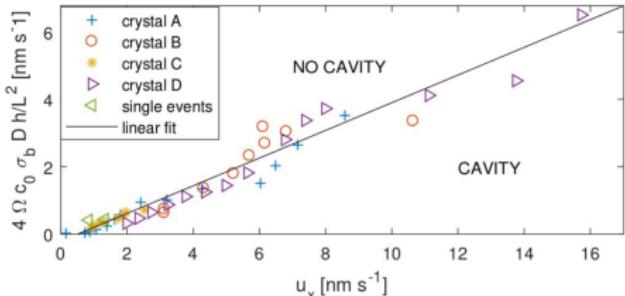
$$\begin{aligned}\pi r^2 J_k &= 2\pi r \zeta_c J_d(r) \\ \pi r^2 \frac{u_{Cz}}{\Omega} &= -2\pi r \zeta_c D \frac{dc}{dr}, \\ \frac{u_{Cz}}{4\Omega} (L^2 - r^2) &= \zeta_c D(c(L) - c(r))\end{aligned}$$

Cavity formation criterion: $c(r = 0) \leq c_0$

$$u_{Cz} \geq 4\Omega c_0 \sigma_b D \frac{\zeta_c}{L^2}$$

$$\sigma_b = c(L)/c_0 - 1$$

Non-equilibrium phase diagram



(a)

Experiments (a) & Theory (b)

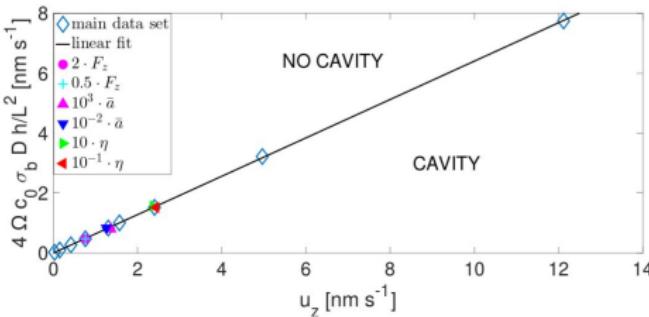
Linear pre-factor < 1

u_{cz} vs u_{cx}

Assumption $\tilde{\gamma} \sim 10^2 \text{ J m}^{-2}$

No influence of

- force / weight, potential amplitude
- BC thickness ζ_b
- viscosity



(b)

Lignes directrices

- 1 Static Wetting of liquids and Solids
- 2 Dynamics of wetting
- 3 Consequences of singular anisotropy
 - Experimental evidences
 - 2D SOS KMC
 - Dewetting of thin films: KMC vs model
- 4 Wetting potential
 - Mesoscopic Continuum thin film model
 - Derivation of the TL Boundary Condition
 - Accelerated mass shedding
 - KMC study of magic heights
 - Conclusion
- 5 Immersed solids
 - Introduction
 - Thin film model
 - Pressure solution
 - Growth: cavity formation
 - Conclusion
- 6 Conclusions

Conclusion

Summary:

- Derivation of a thin film lubrication model for dissolution/growth + confinement
- Pressure solution of a single contact
Depends on the repulsive potential profile
- Confined growth
Cavity formation: initial stage of growth rims

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Wetting and dewetting of liquid and solid films

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- Dewetting of solid films:

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- Immersed solids

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