Growth modes/Wetting and dewetting

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Outlook

I/ A few concepts

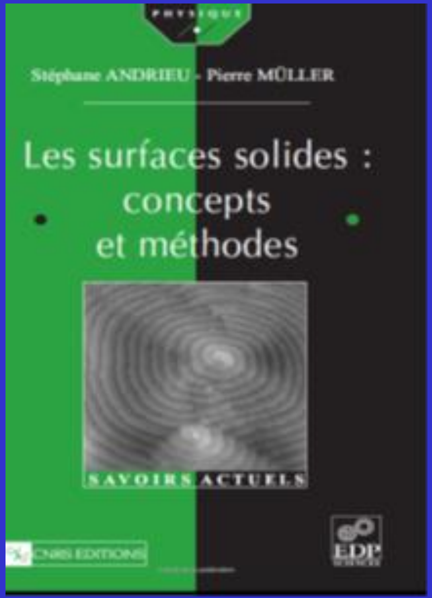
II/ Imaging the surface dynamics

III/ Wetting

IV/ Growth modes

V/ Dewetting

Reviews



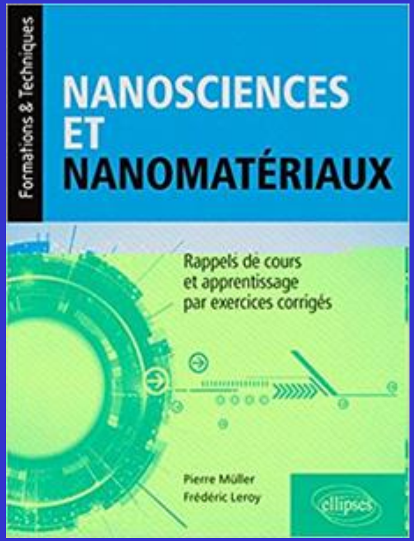
C. Misbah, O. Pierre-Louis, Y. Saito, « *Crystal surfaces in and out of equilibrium* »
Rev. Modern Physics, 82 (2010) 981-1040

P. Müller, A. Saul, « *Elastic effects on surface physics* »
Surface Science Reports, 54 (2004) 157-258

M. Giesen, « *Step and island dynamics at solid/vacuum and solid/liquid interfaces* »
Progress in Surface Science 68 (2001) 1-153

J. Hyeong-Chai, E. Williams, « *Steps on surfaces: experiments and theory* »
Surface Science Reports 34 (1999) 171-294

Books



B. Mutaftschiev, « *The atomic nature of crystal growth* » Springer 2001

A. Pimpinelli, J. Villain, Physics of crystal growth, Alea Savlay 1998

I. Markov, « *Crystal growth for beginners* » World Scientific 1995

Y. Saito, « Statistical physics of crystal growth » World Scientific 1996

H. Ibach, « *Physics of surfaces and interfaces* » Springer 2006

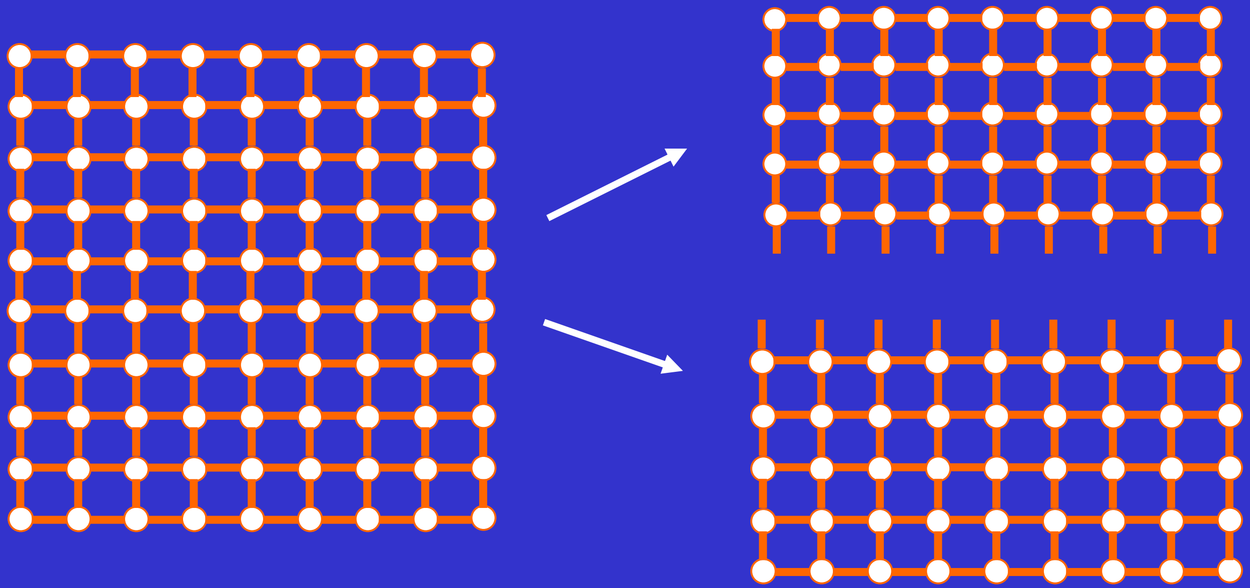
S. Andrieu, P. Müller, « *Les surfaces solides: concepts et méthodes* » CNRS 2005

P. Müller, F. Leroy, « *Nanosciences et nanomatériaux: rappels de cours et apprentissage par exercices corrigés* » Ellipse, 2018, 300 pages

I/ A few concepts

Concept of ideal flat surfaces (by cleavage process)

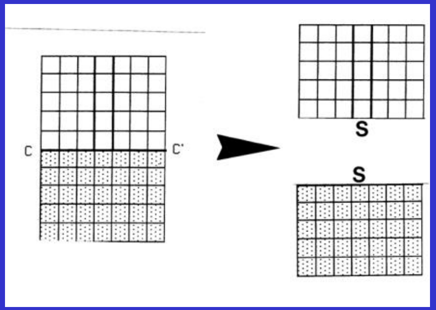
A surface is created by cutting a crystal



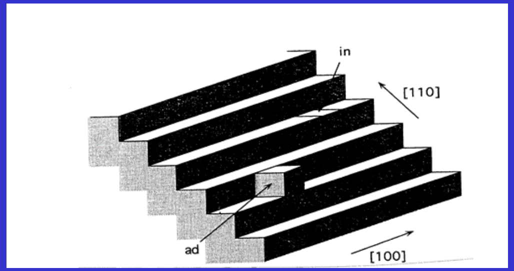
Energetic cost to cut the crystal: W

Surface energy density: $\gamma = W/2S$

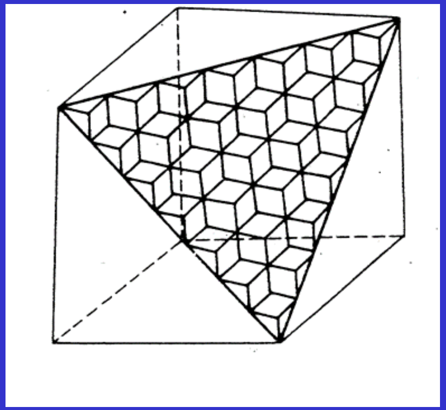
For a Kossel crystal
(First neighbors interactions)



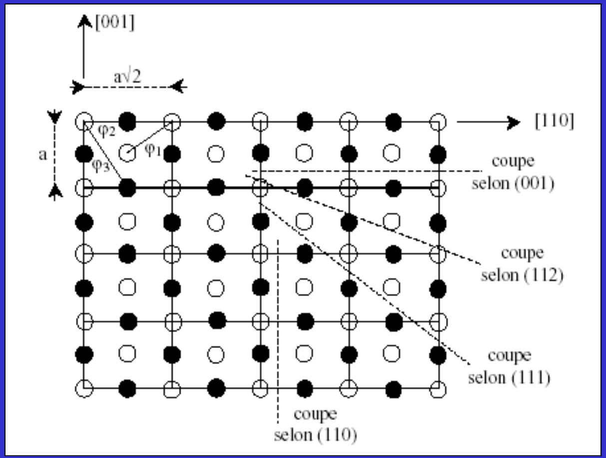
$\gamma = \phi / 2a^2$



$\gamma = 2\phi / (2\sqrt{2})a^2$



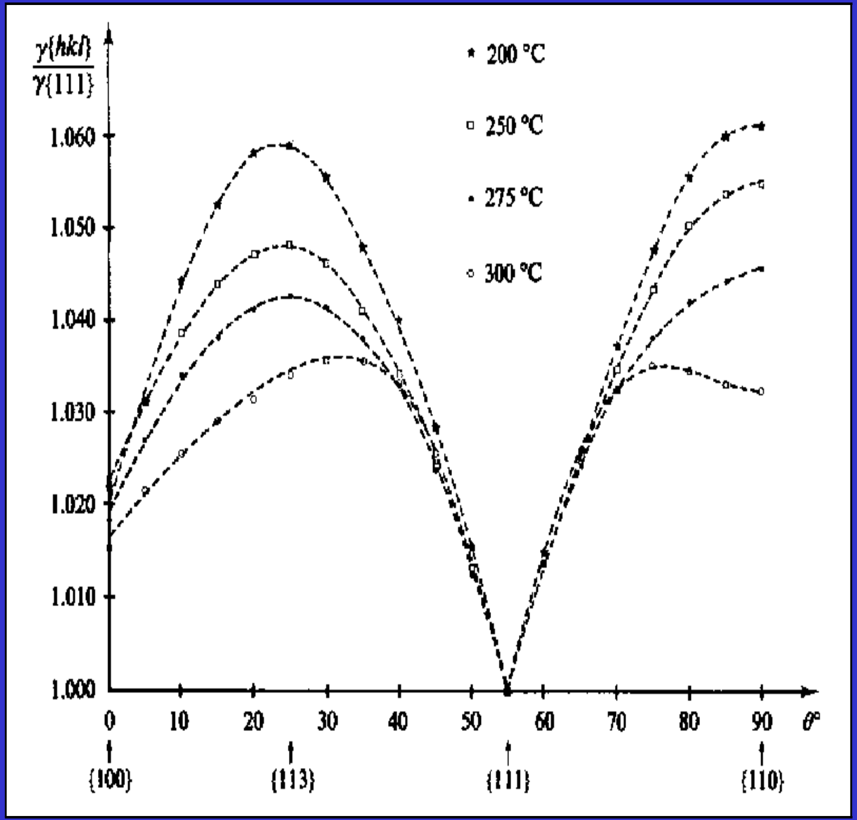
$\gamma = 3\phi / (2\sqrt{3})a^2$



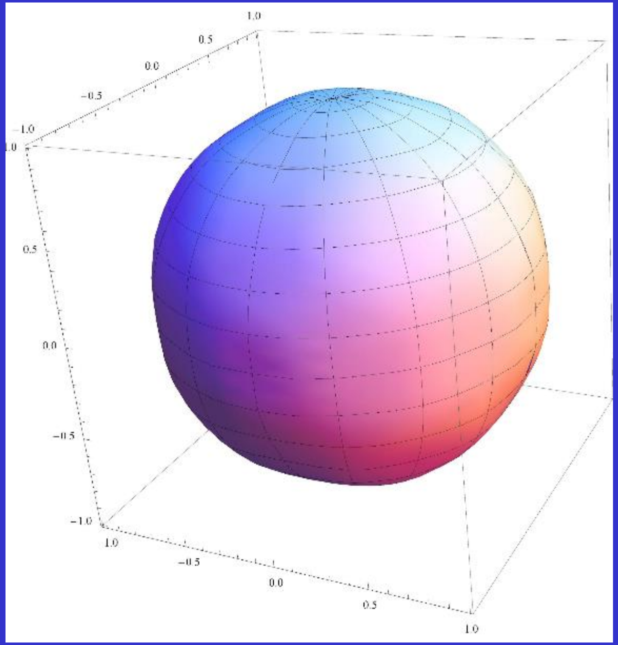
Generalization:

$$\gamma_{hkl} = \frac{W_{hkl}}{2A_{hkl}} = \frac{1}{2A_{hkl}}[n_1(hkl) + n_2(hkl) + n_3(hkl) + \cdots]$$

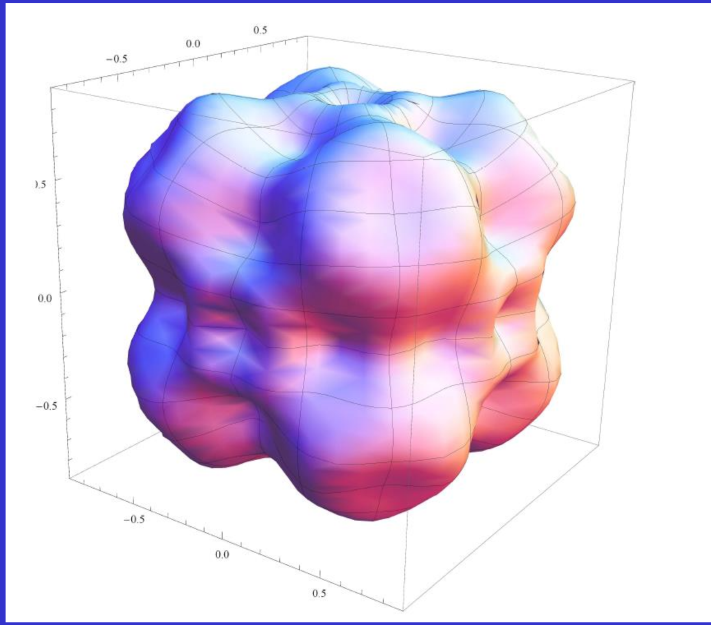
Lead on graphite:
J.J. Metois, J.J. Heyraud,
. Sci 128 (1983) 334.



The gamma plot



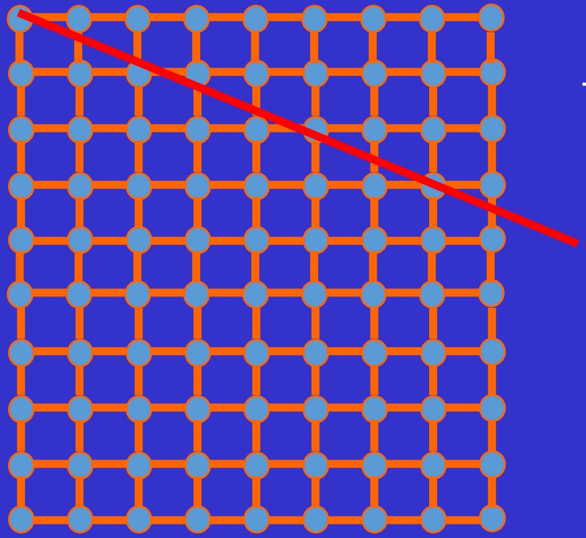
Quasi-isotropic gamma-plot



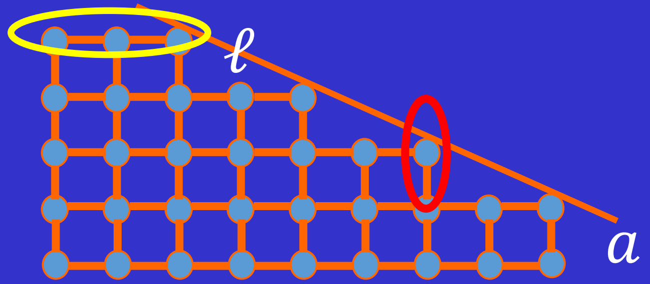
Anisotropic gamma-plot

The concept of vicinal (stepped) surfaces

Vicinal surface:

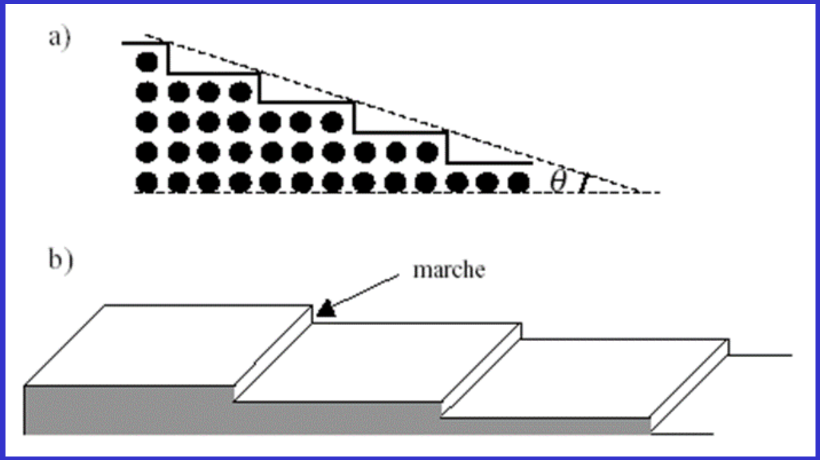


flat terraces separated by steps



Vicinal angle: $\tan\theta = a/\ell$

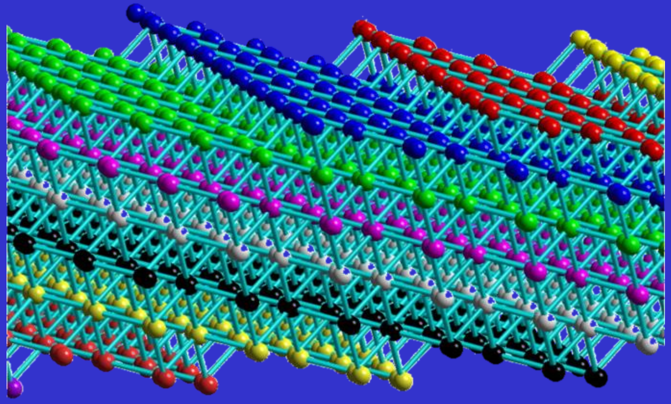
$p = \tan\theta$ step density



$$\beta(\theta) = \gamma_0 + \beta_1 |p| + \beta_3 |p|^3$$

β_1 Step energy

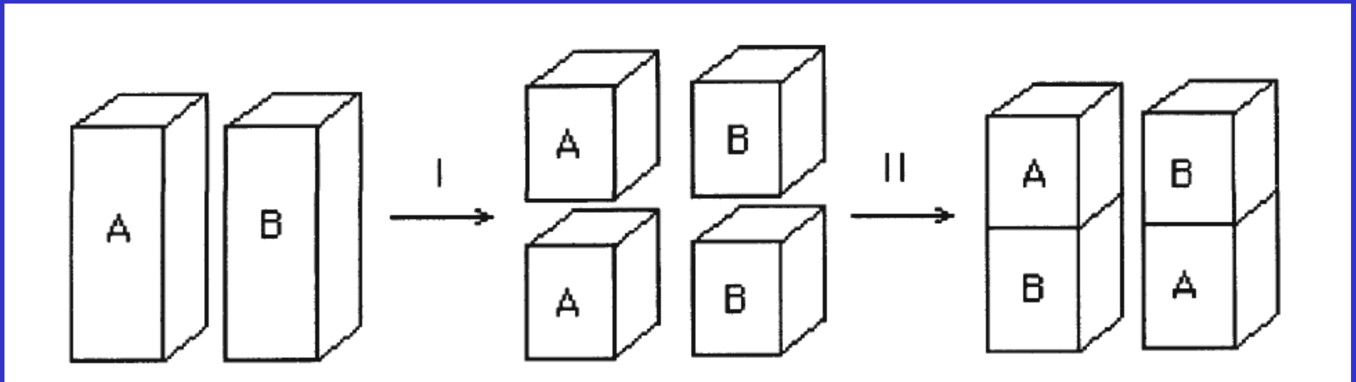
β_3 Step-step interaction



Si(314)

Adhesion energy and Dupre relation

A. Dupré, *Théorie mécanique de la chaleur* (Gauthier-Villard, 1869), p. 369



Per unit area $2\gamma_A + 2\gamma_B$ -2β $= 2\gamma_{AB}$

Dupre'relation

$$\gamma_A + \gamma_B - \beta = \gamma_{AB}$$

With broken bonds with only first neighbours model

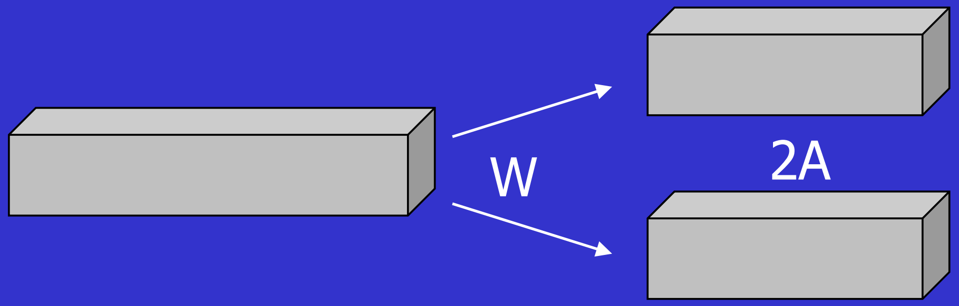
$\beta = \frac{\Phi_{AB}}{a^2}$ Adhesion energy

$\gamma_i = \frac{\Phi_i}{2a^2}$ Surface energy (density)

$\gamma_{AB} = \frac{\Phi_i}{2a^2} + \frac{\Phi_i}{2a^2} - \frac{\Phi_{AB}}{a^2}$ Interfacial energy

Surface creation

Increase area upon creation (cleavage)



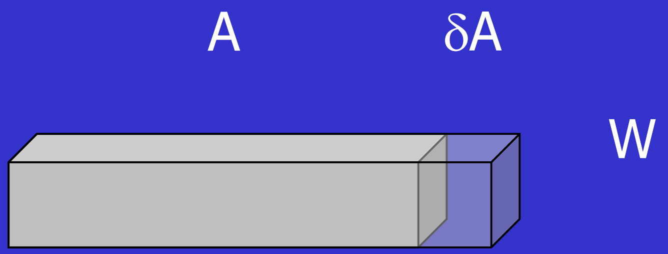
Surface energy

- **Work per surface area :**

  γ **[J/m^2] = W/2A**

- **Scalar, anisotropic**
- **Origin : broken bonds**

Increase area upon stretching (deformation)



Surface stress

- **Work per surface area**

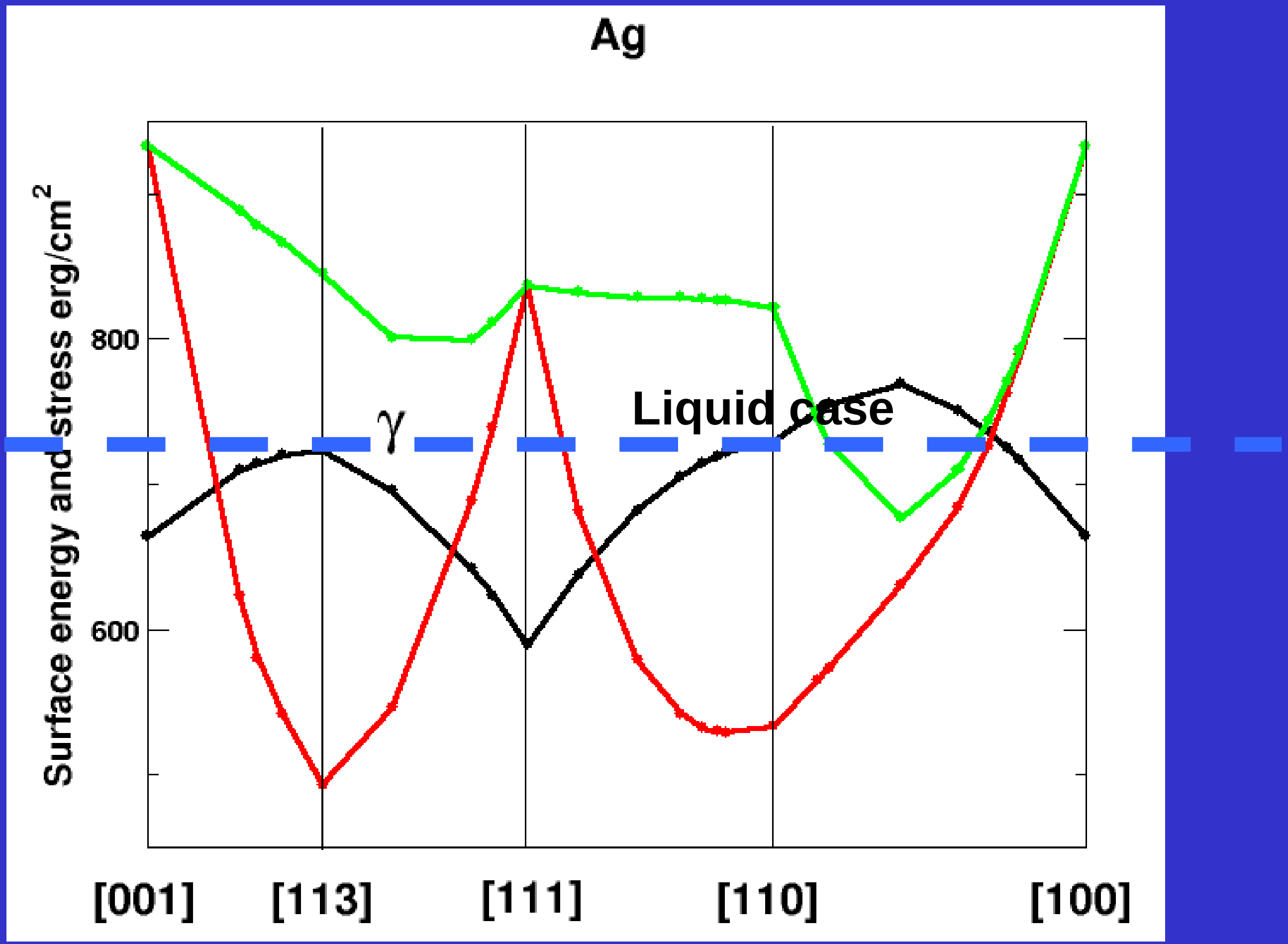
  s_{ij} **[mJ/m^2] = W/**δ**A**

- **Tensor, anisotropic**
- **Origin : modification of the bond strength**

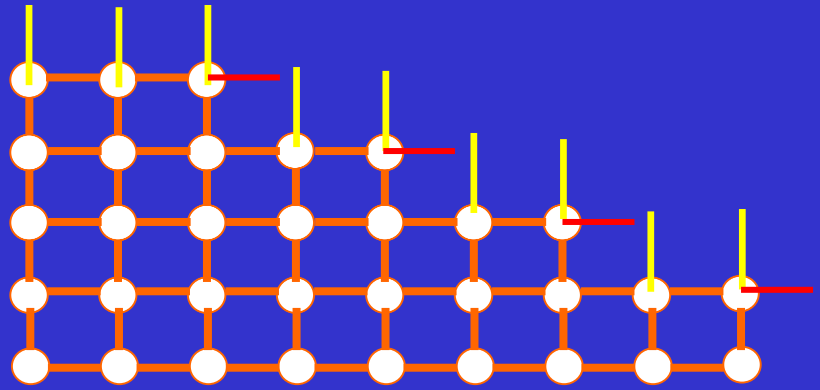
For liquids there is no need to distinguish them. The quantity $s=\gamma$ is called surface tension

P. Müller, A. Saul, « *Elastic effects on surface physics* » Surface Science Reports, 54 (2004) 157-258

Surface energy versus surface stress

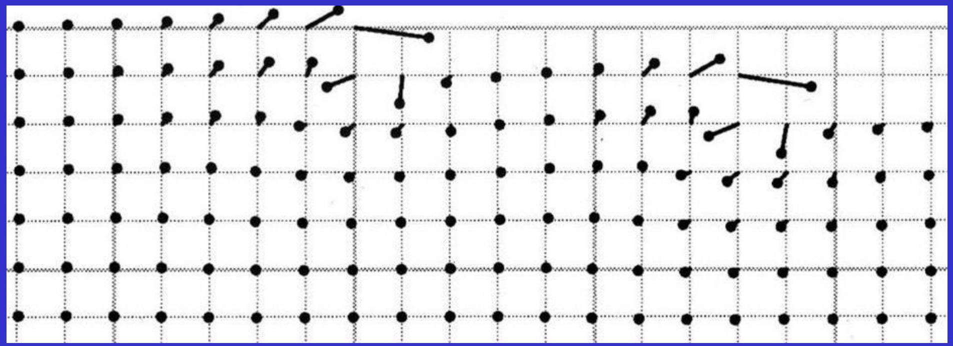


- Surface energy
  - one branch (scalar)
  - minima at low index



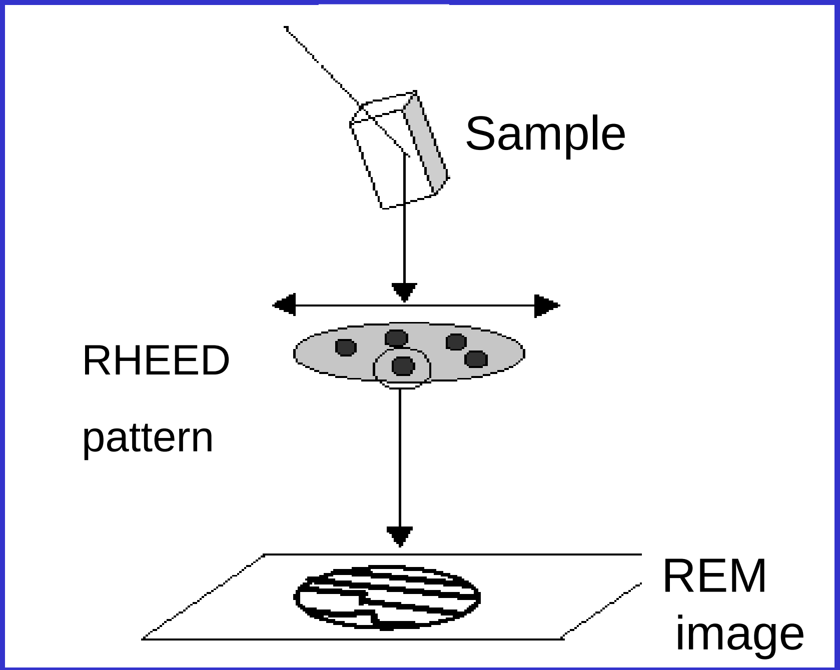
- Surface stress
  - two branches
  - diagonal at high symmetry points
  - maxima at low index orientations

P. Müller, A. Saul, *« Elastic effects on surface physics »* Surface Science Reports, 54 (2004) 157-258



II/ Imaging the surface dynamics

Reflection Electron Microscopy (REM)



-e^- energy typically 20 keV

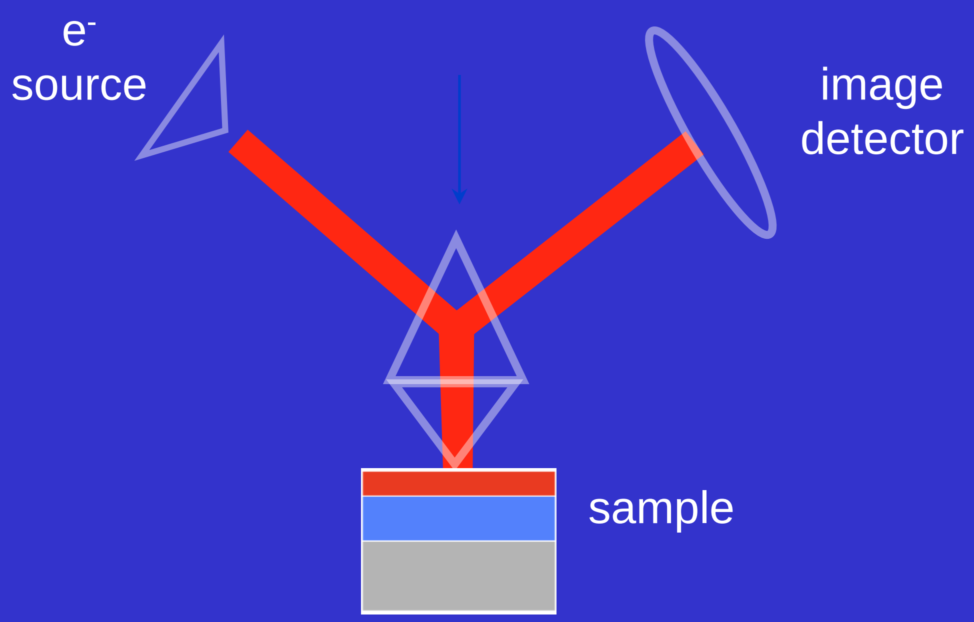
-Surface sensitive (grazing incidence, image distortion)

- in-situ real time 0.1s/image

-5 nm lateral resolution

-Atomic vertical resolution

Low Energy Electron Microscopy (LEEM)



-e^- energy typically < 20 eV

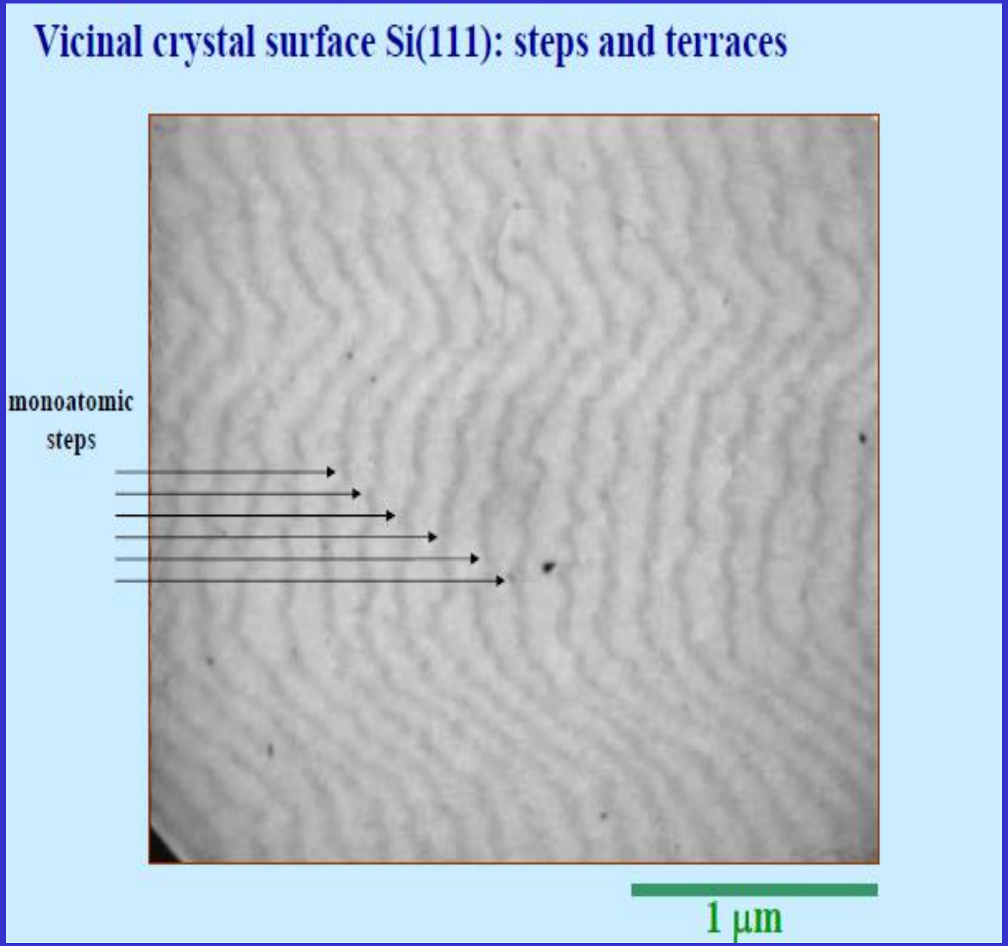
-Surface sensitive (normal incidence, no image distorsion)

- in-situ real time 0.1s/image

-10 nm lateral resolution

-Atomic vertical resolution

Typical REM image of a vicinal surface



Typical LEEM image of a Si (001) surface

III/ Wetting

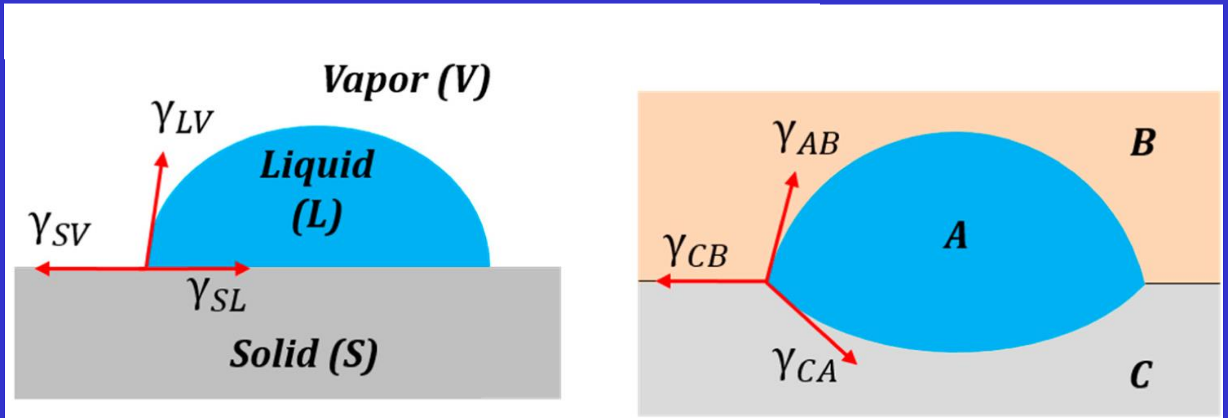
Wetting: Case of a liquid droplet deposited on a solid or a liquid

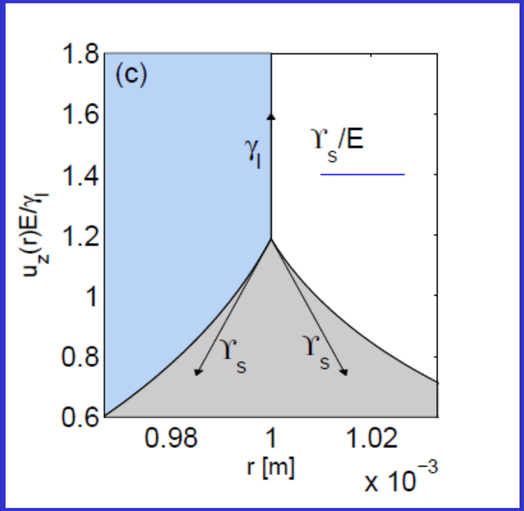
Young equation obtained by minimising the total surface energy

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

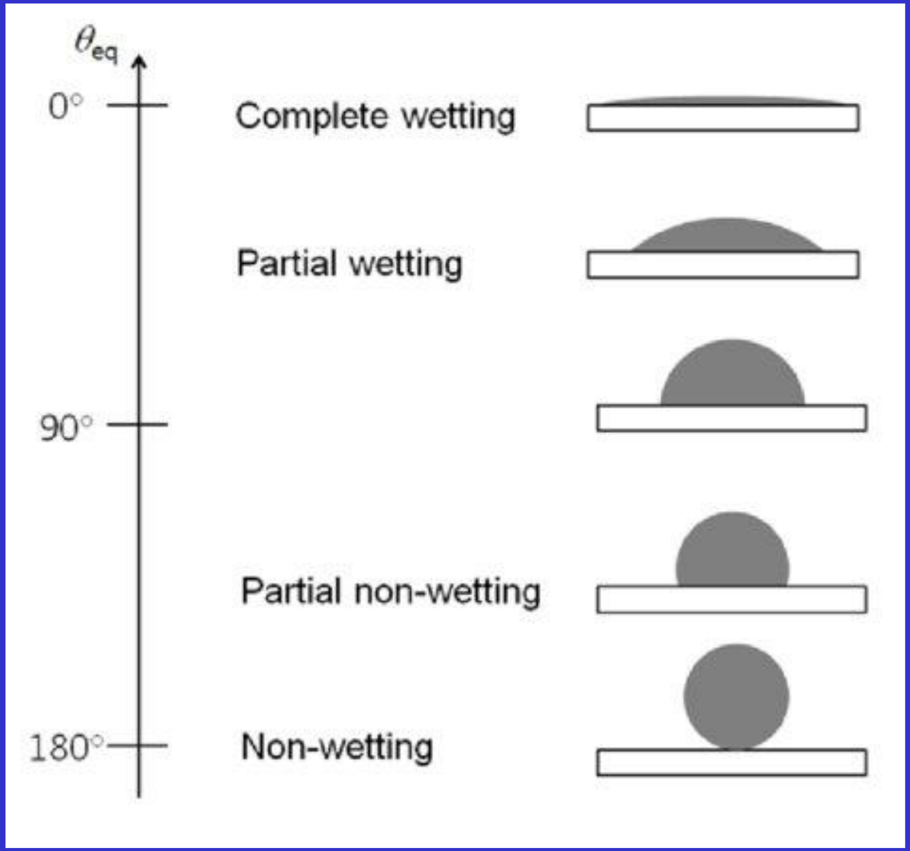
θ is the Contact (or wetting) angle

Looks like a force projection but … $\gamma_{sv} = \gamma_{lv}\cos\theta + \gamma_{sl}$



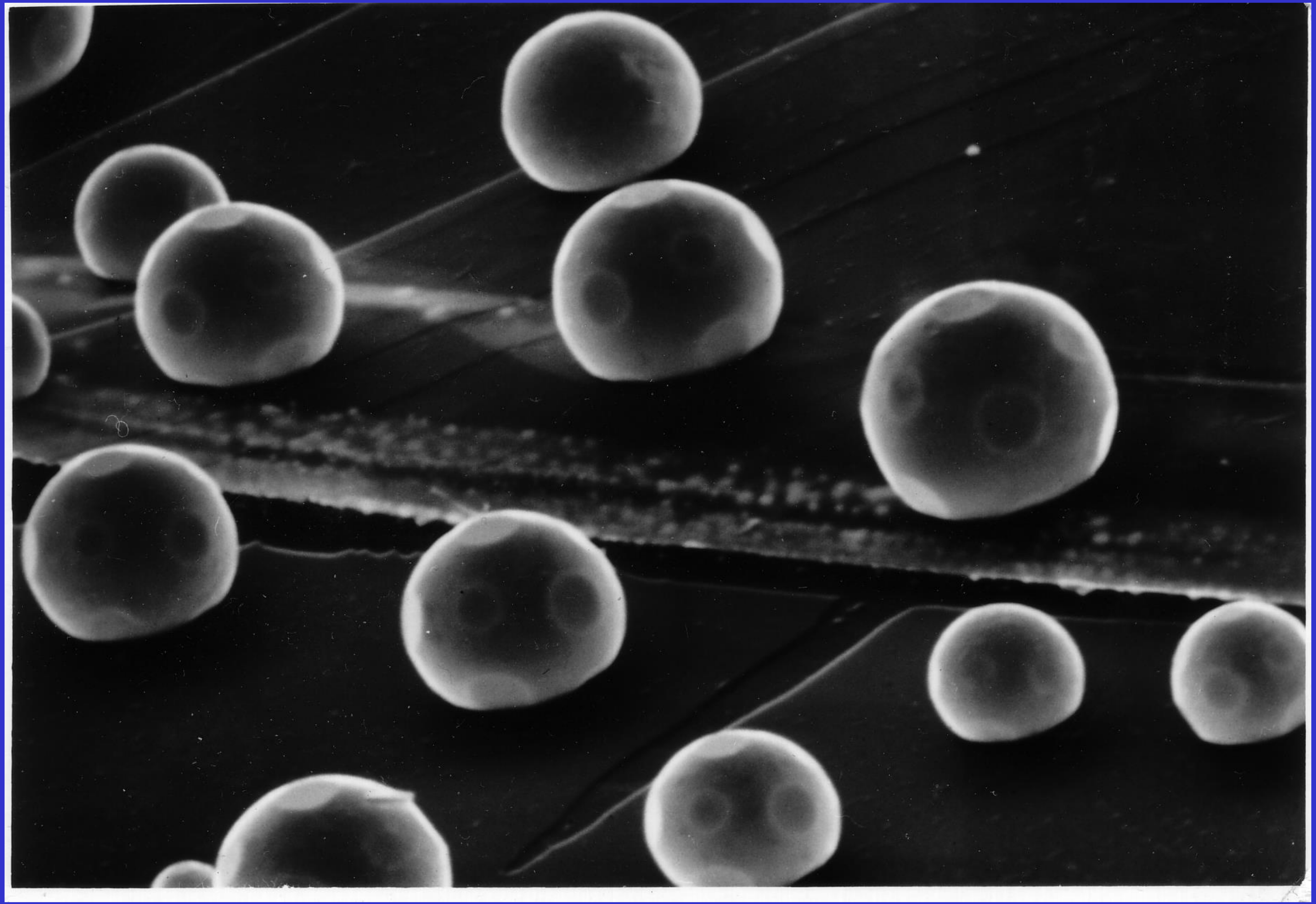


Liquid droplet on soft matter, with surface stresses



Adhesion energy: $\beta = \gamma_{lv}(1 - \cos\theta)$

Equilibrium shape of a crystal on a solid substrate



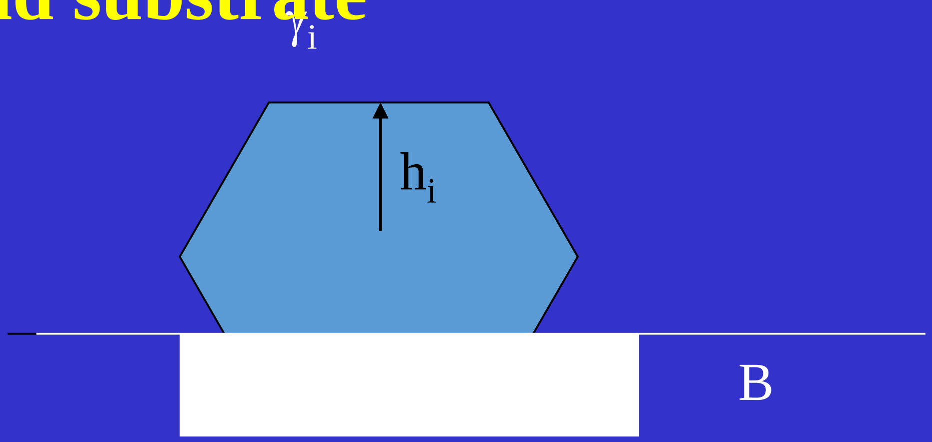
Lead on graphite

J.J.Métois, J.C. Heyraud

Surface Science 128 (1983) 334

- Shapes do not depend on the crystal volume
- Truncated shapes (with respect to free crystals)
- Here coexistence of rounded face and flat facets

Equilibrium shape of a crystal on a solid substrate



$$\Delta F = -n\Delta\mu + \sum_i \gamma_i S_i + \left(\gamma_{AB} - \gamma_B\right) S_{AB}$$

G.Wulff, Z.Krist. 34 (1901) 446

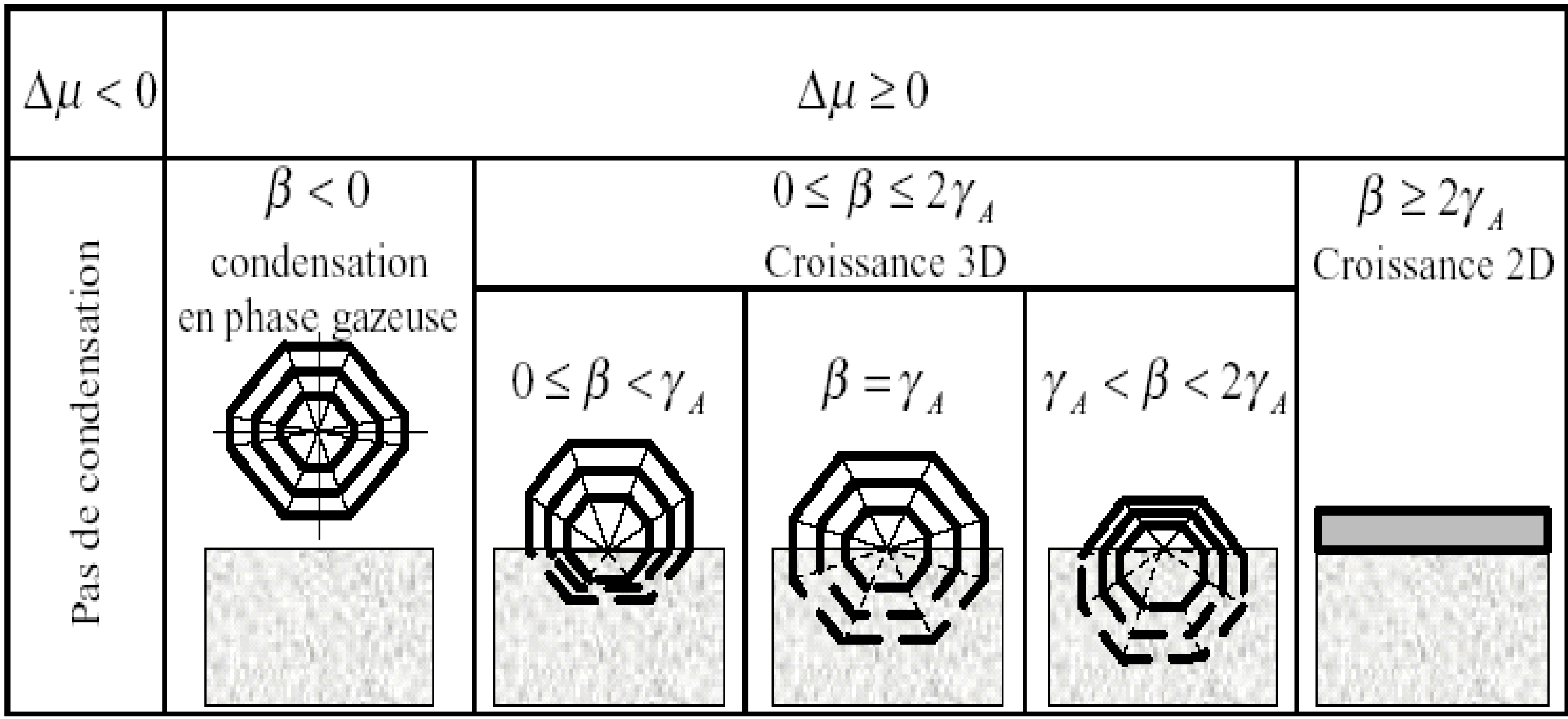
$d\Delta F = 0$ leads to the **Wulff-Kaishew theorem**

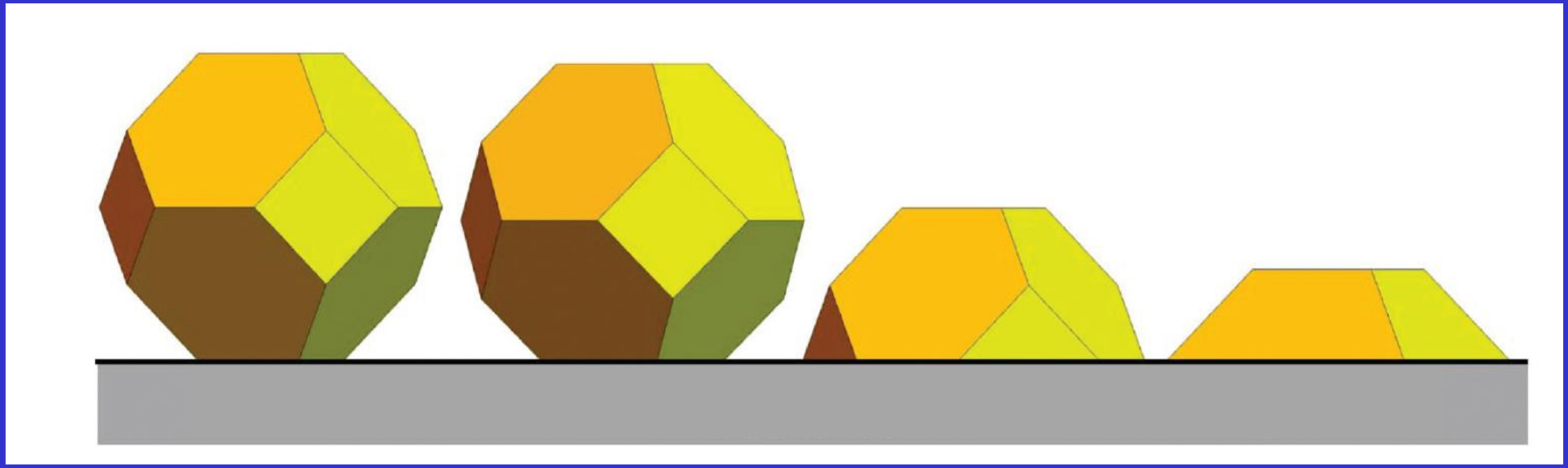
$$\frac{\Delta\mu}{2v} = \frac{\gamma_i}{h_i} = \frac{\gamma_{AB} - \gamma_B}{h_{AB}} = \frac{\gamma_A - \beta}{h_{AB}}$$

R.Kaishew, Commun. Bulg. Acad. Sci. 1 (1950) 100

Wulff-Kaishew theorem

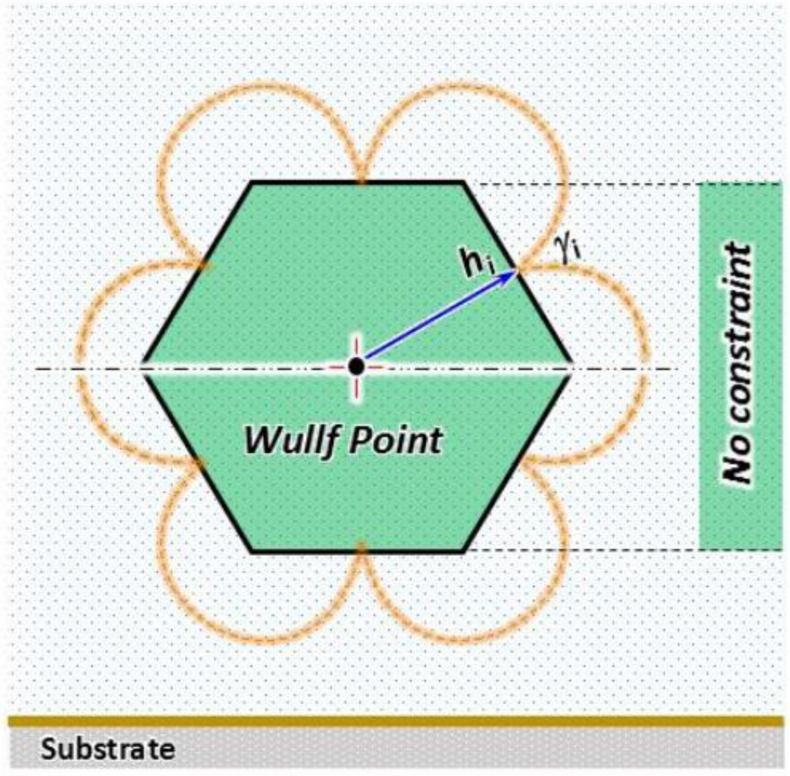
$$\frac{\Delta\mu}{2v} = \frac{\gamma_A}{h_A} = \frac{\gamma_A + \gamma_{AB} - \gamma_B}{h_A + h_{AB}} = \frac{2\gamma_A - \beta}{h_A + h_{AB}}$$





Synthesis

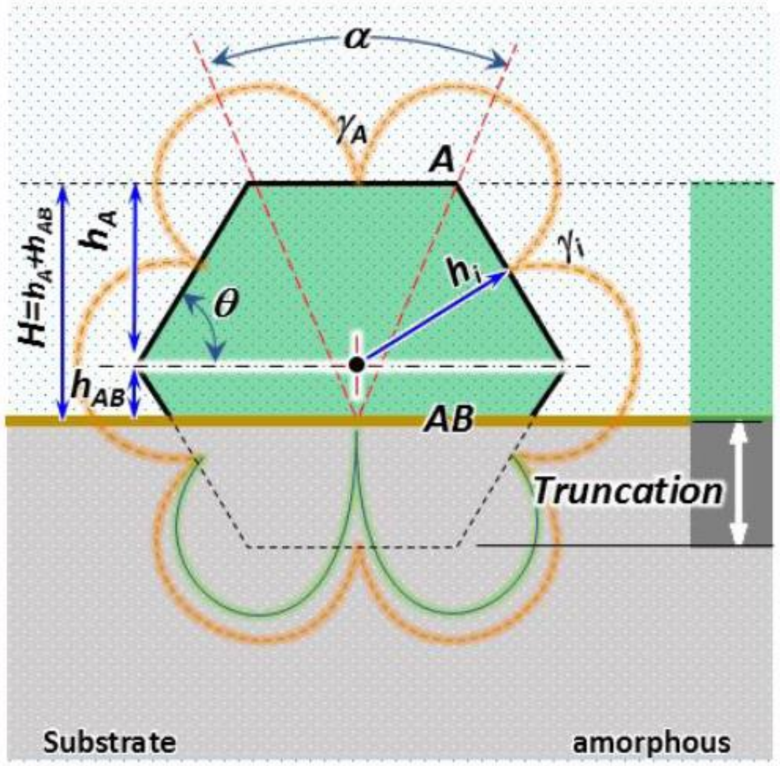
Free equilibrium shape



Wulff theorem

G.Wulff, Z.Krist. 34 (1901) 446

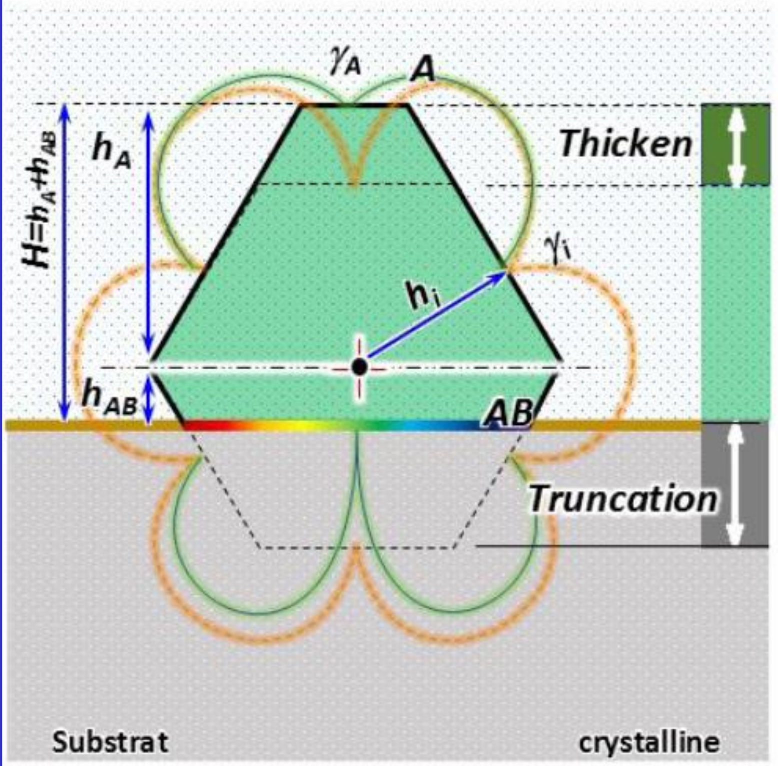
Deposited equilibrium shape
(without elasticity)
Truncated shape



Wulff-Kaishew theorem

R.Kaishew, Commun. Bulg. Ac. Sci. 1 (1950) 100

Deposited equilibrium shape
(with elasticity)
Thickening induced by elasticity

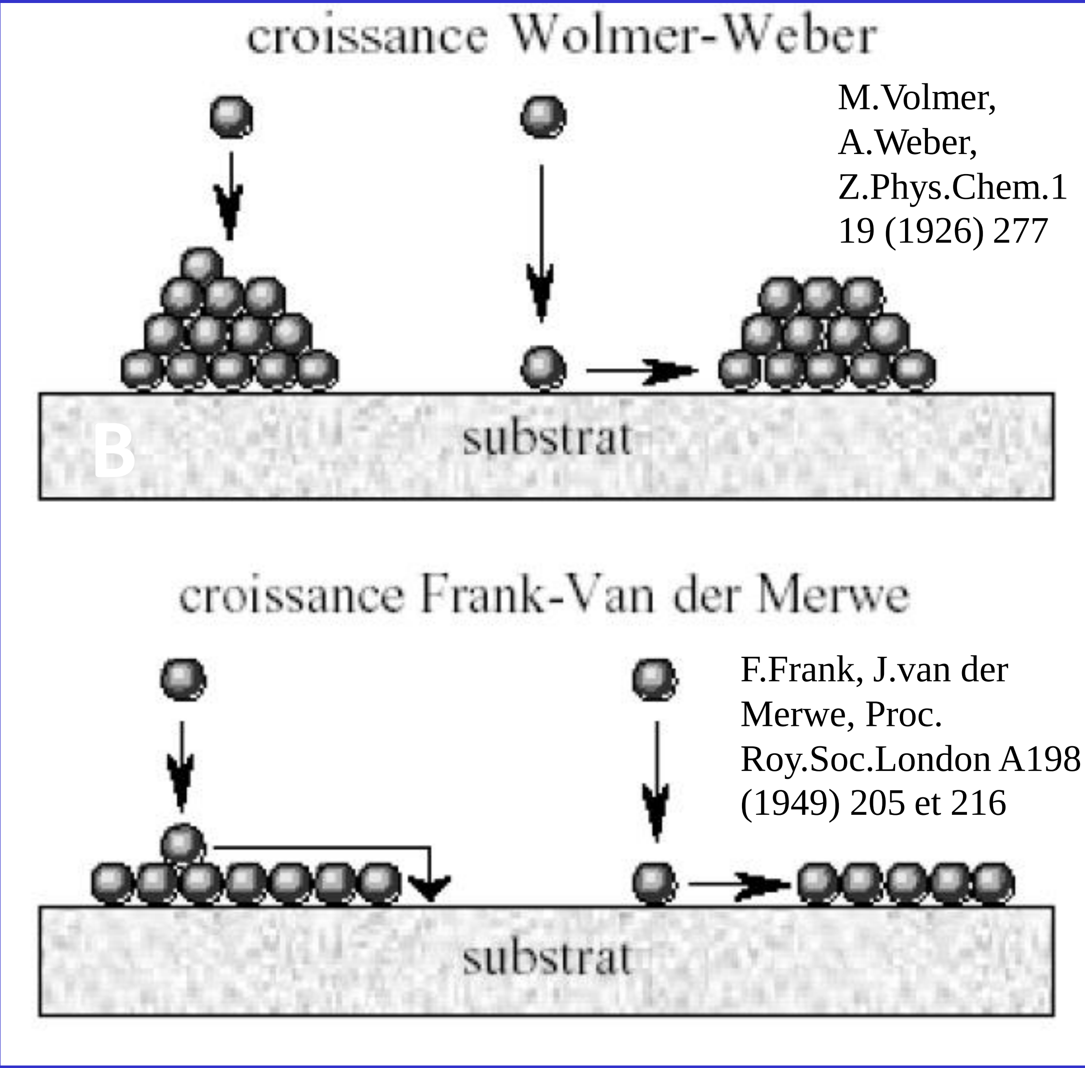


Generouslized Wulff-Kaishew theorem

P.Müller, R.Kern, Surf. Sci. 457 (2000) 229-253

IV/ Growth modes

Growth modes



Bauer criterion

E. Bauer Z. Krist. 110 (1958) 372

3D growth ⟶ $\gamma_A + \gamma_{AB} > \gamma_B$

The system mimimizes its energy with large areas of bare B

2D growth ⟶ $\gamma_A + \gamma_{AB} < \gamma_B$

The system mimimizes its energy by covering B

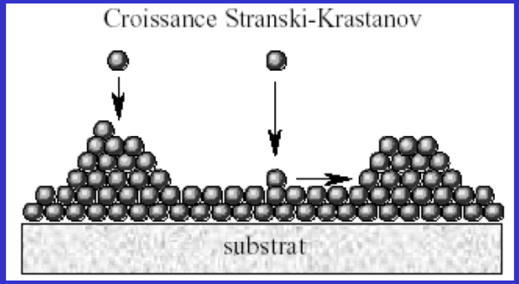
Growth conditions depend on the sign of the so-called Wetting factor

$$\Phi = \gamma_A + \gamma_{AB} - \gamma_B$$

Extension of the Bauer criterion **with elasticity**:

R. Kern, P. Müller, J. Cryst. Growth 146, (1995) 193

But a mixed mode exists the Stranski Krastanov mode (2D then3D)



What is the driving force?

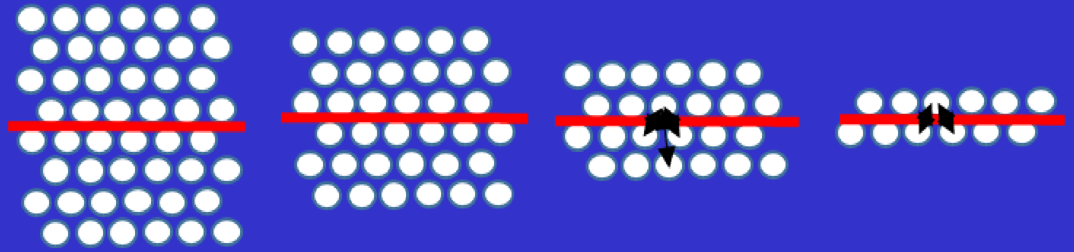
Oscillating Φ ??

Vanishing Φ ?

Orginal work for polar crystals :
L. Stranski, L. Krastanov, Sitz. Ber. Akad. Wiss. Wien. 146 (1938)

Actually three ingredients:

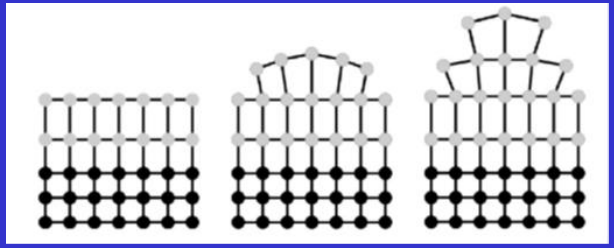
- $\phi < 0$ but decreasing with z (the number of bonds to break varies)



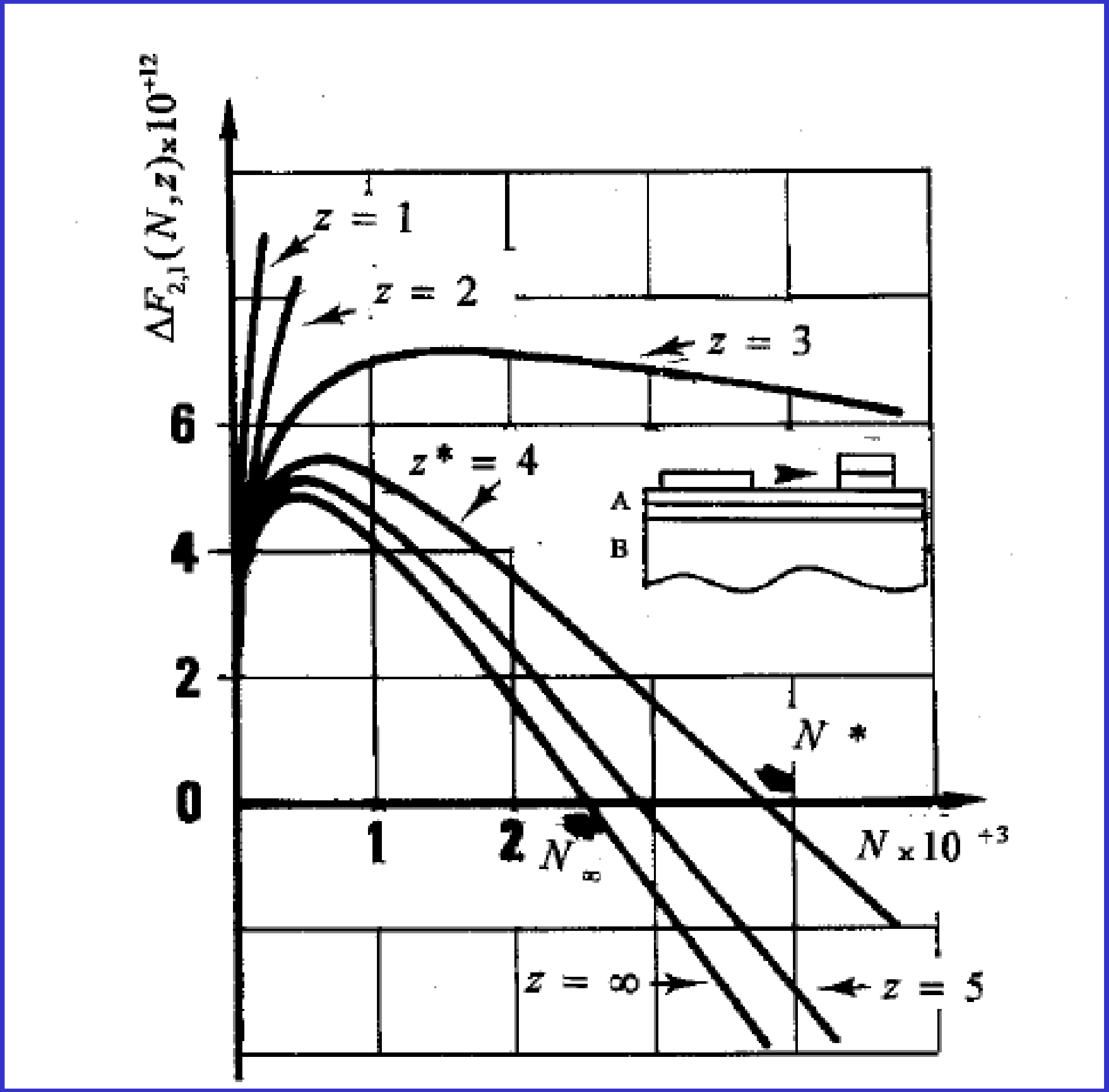
- Elastic energy stored by the 2D mifitted layers

$$\Delta W_{\mathrm{el}} = \frac{E_A}{1 - \nu_A} m^2$$

- Elastic relaxation of the islands (and its substrate)



Application for: Si(111)/Ge(111) on z 2D layers



$$\Delta F = F_{3D} - F_{2D}$$

$$\Phi = -128\, erg.cm^{-2}$$

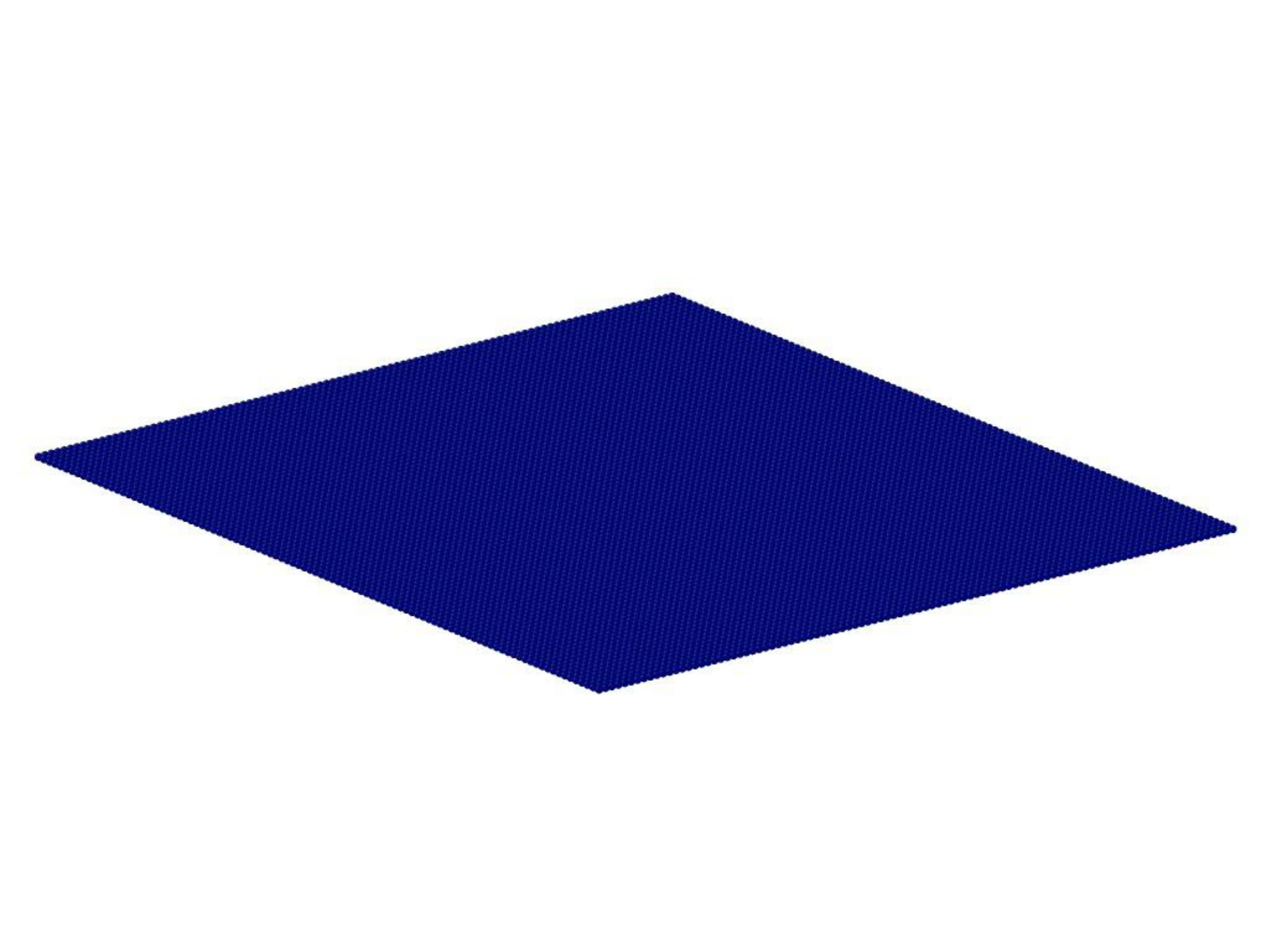
m=-0.035

ΔF becomes <0 → 3D growth for z>3

P. Müller, R. Kern, App. Surf. Sci. 102 (1996) 6

$\xi=1$

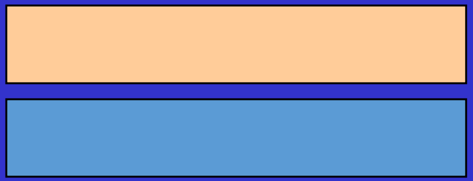
KMC Simulation of 2D Growth



$$\Phi < 0$$

Leem movie of Frank-van der Merwe growth

Pb on Si(111) previously covered by 1 ML of Au



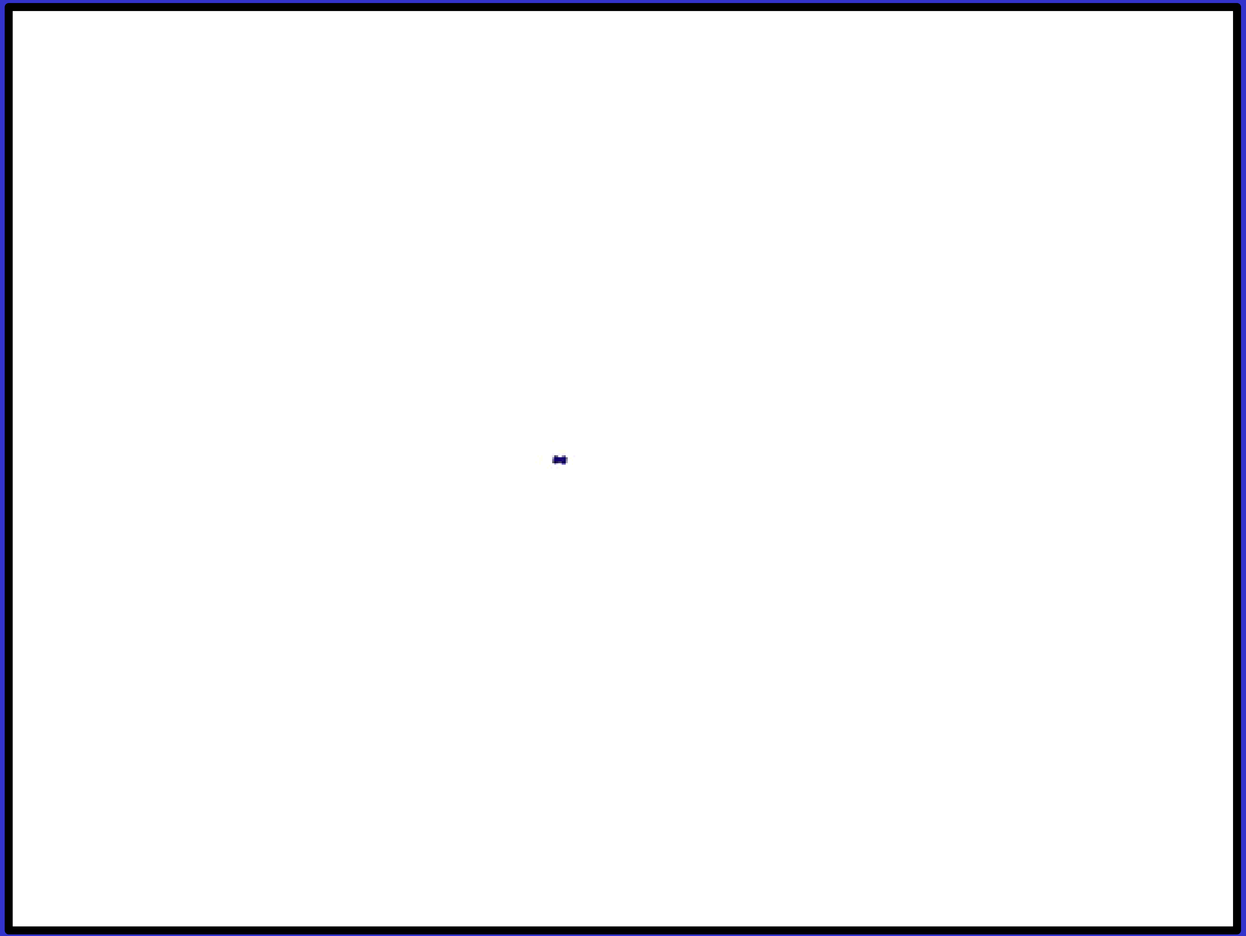
$\Phi < 0$

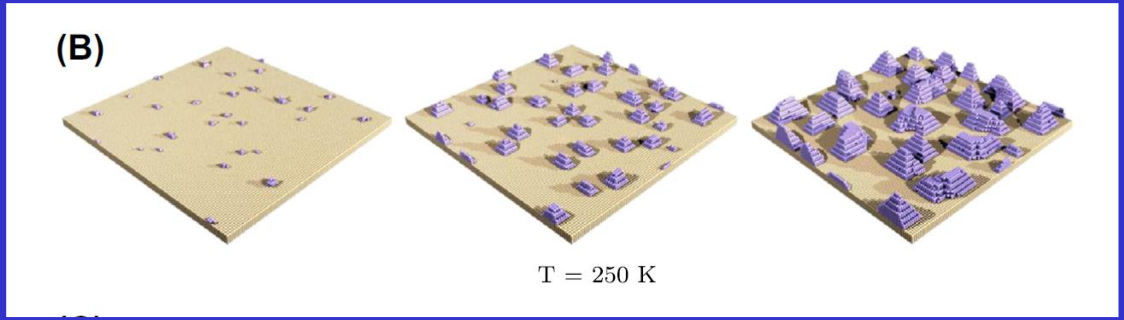
1 ML Au formation
followed by
layer-by-layer
Pb growth

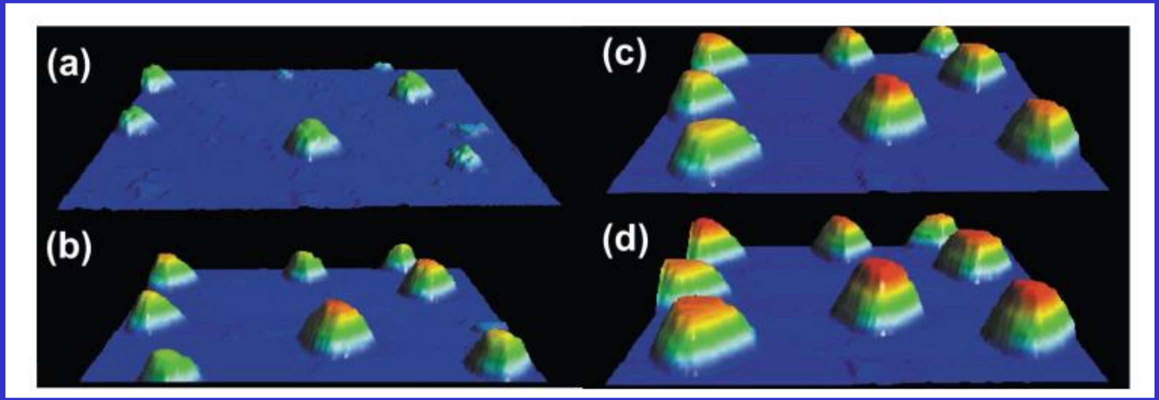
Schmidt et al PRB 62 (2000) 15815

KMC simulation of 3D Growth

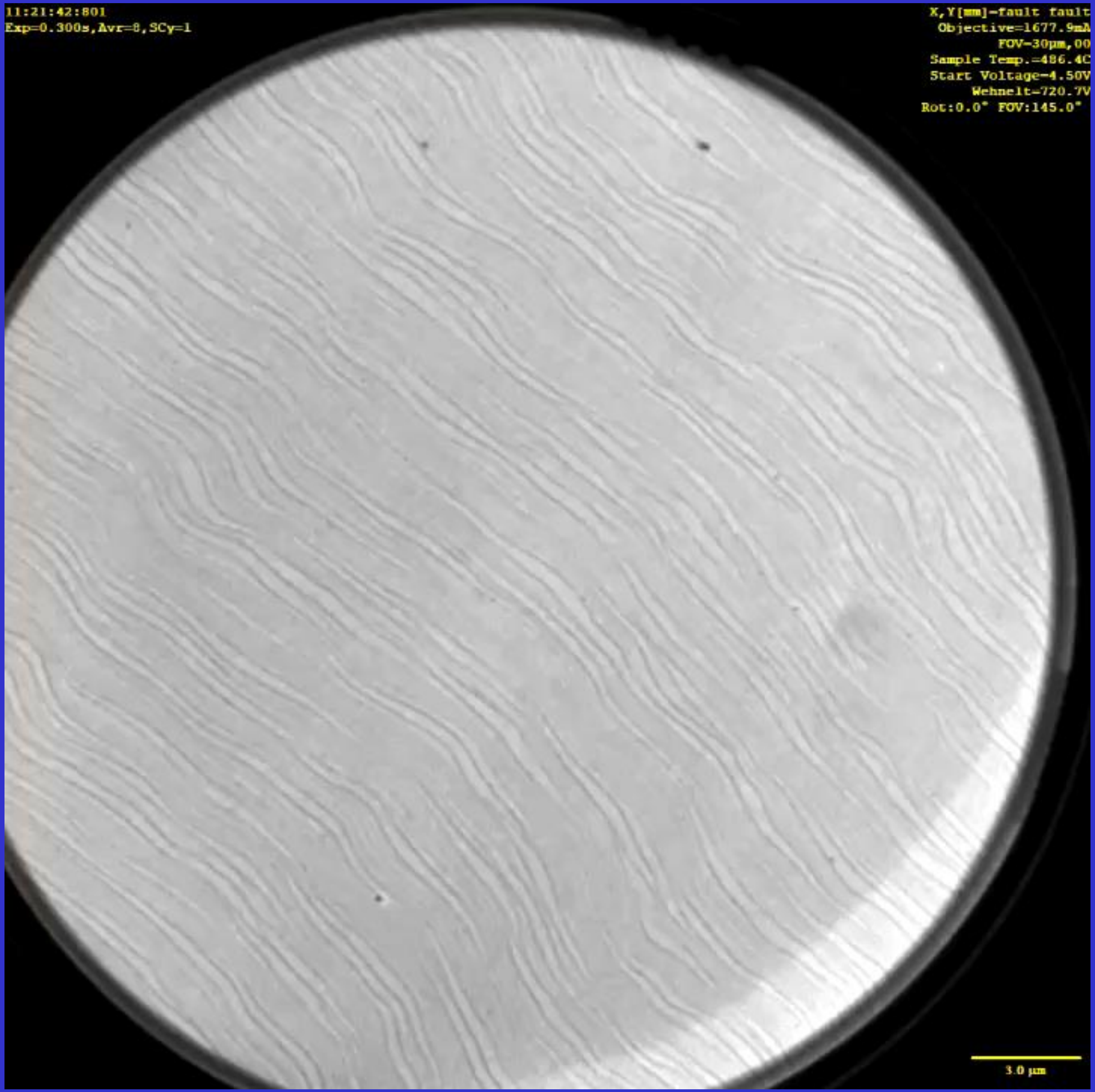
Zepeda-Ruiz Handbook
Crystal growth 2015







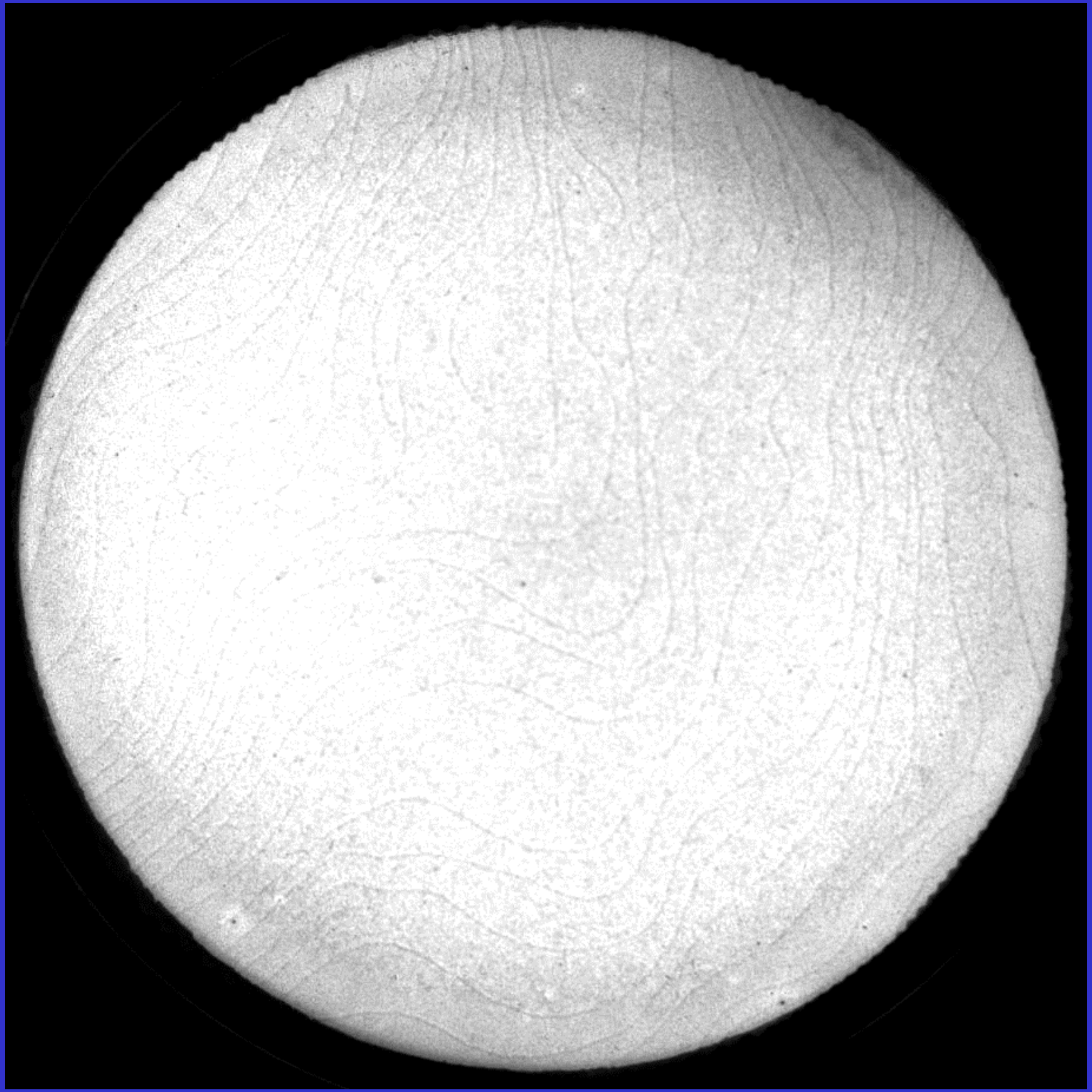
LEEM movie of Stranski Krastanov growth of Au/W(111)



Three 2D layers followed by the growth of 3D dendritic crystals

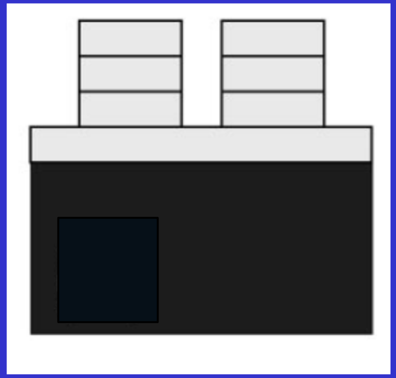
LEEM Movie of Stranski-Krastanov growth of Fe/W(001) at 800 K

2D → 3D transition from a stable pseudomorpic state



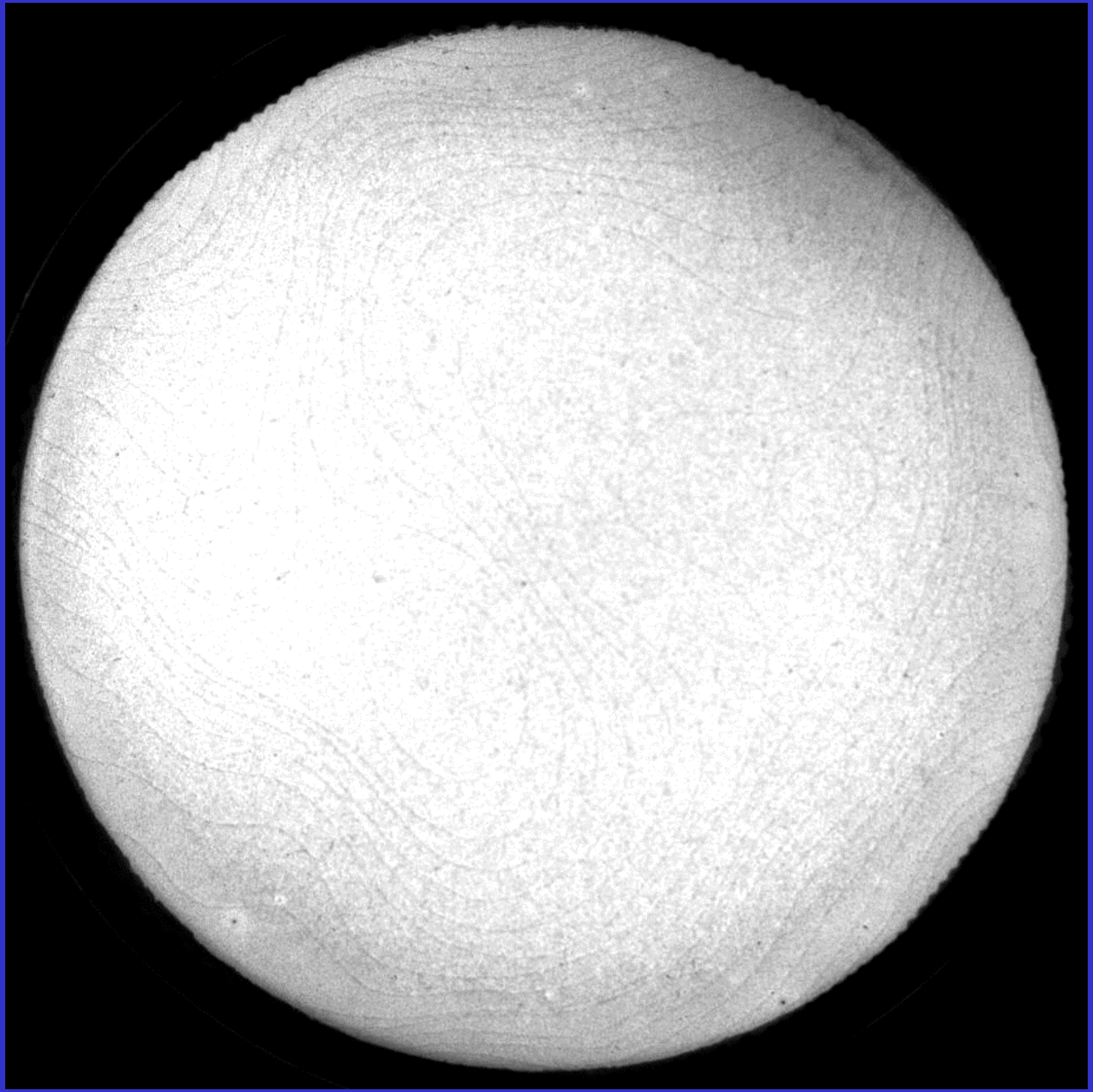
2: 2D layer growth
followed by
3D islands growth

Y. Niu et al. PRB 95 (2017) 064404



Stranski-Krastanov growth of Fe/W(001) at 600 K

2D → 3D transition form metastable pseudomorphic state



1/ 2D growth until 2 ML

2/ 3D nucleation at 3.2 ML

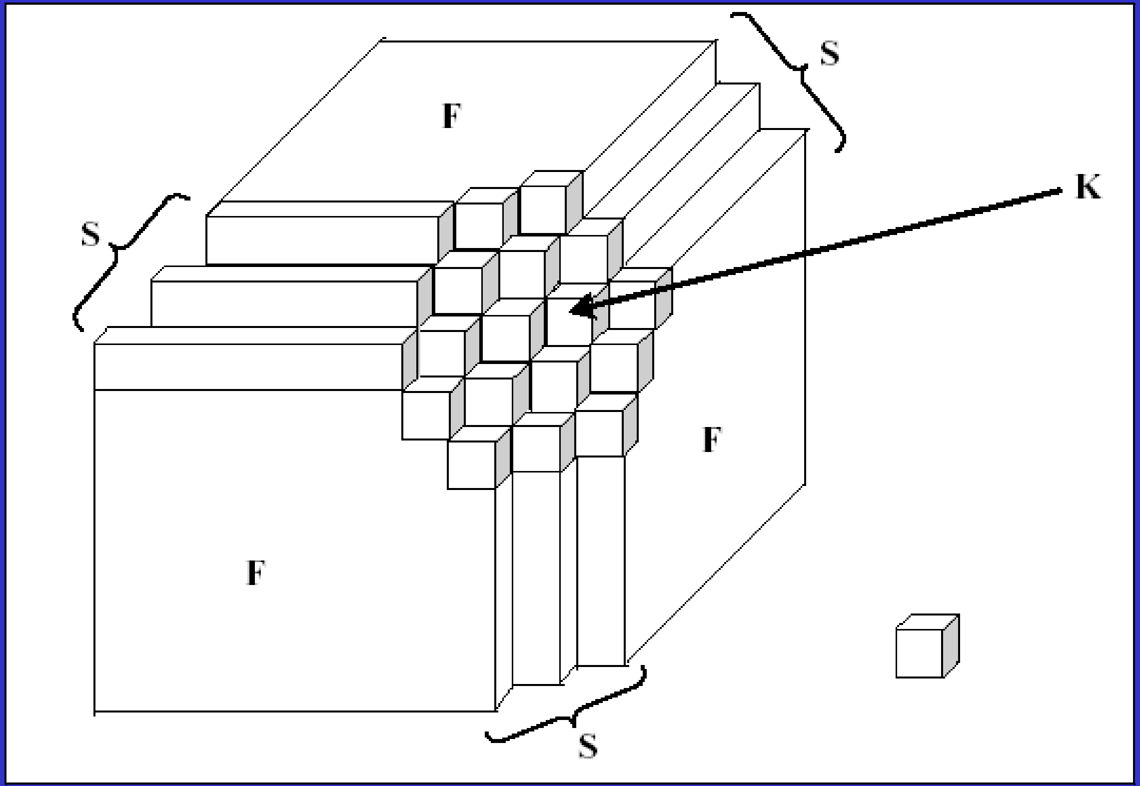
3/ 3D growth consuming material in excess of 2 ML

Y. Niu et al.
PRB 95 (2017)
064404

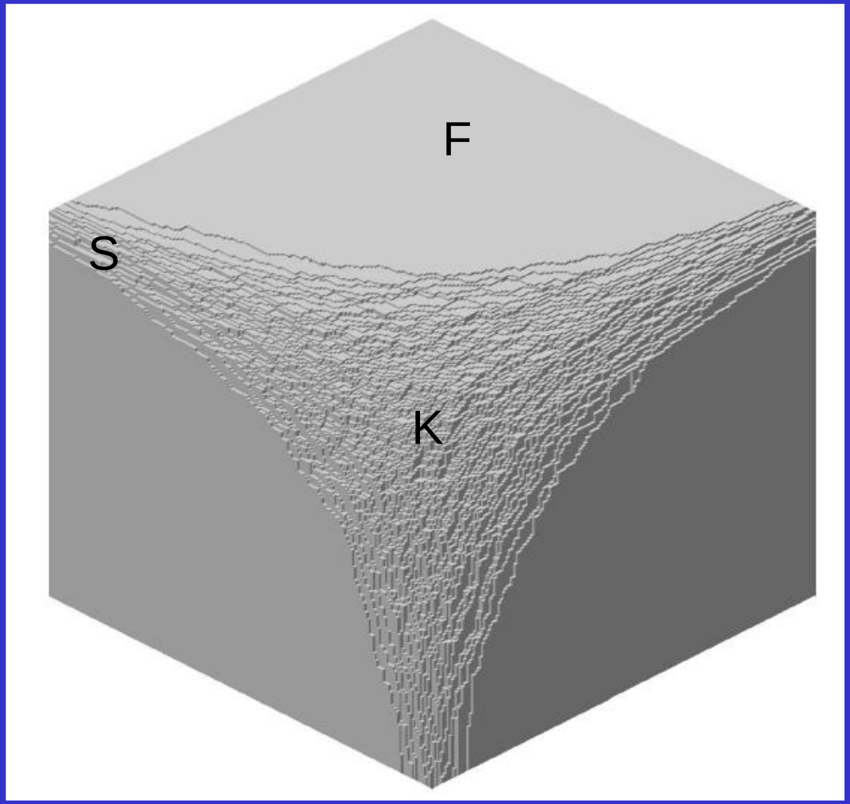
Atomic description of the incorporation of units growth

Kossel crystal

W.Kossel,
Nachrichten der Gesellschaft der Wissenschafften Göttingen Mathematisch-Physikalische Klasse, Band 135 (1927)

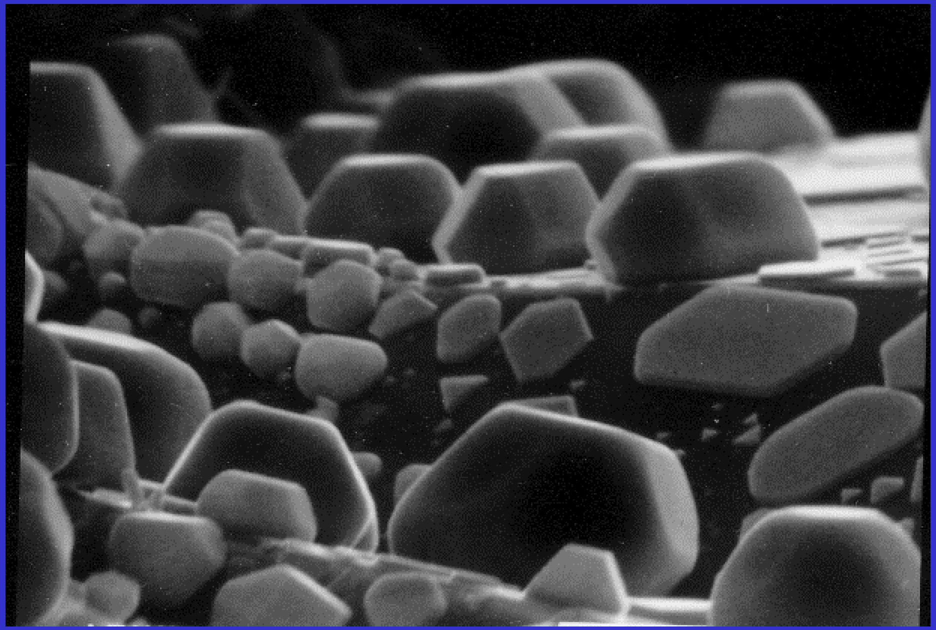


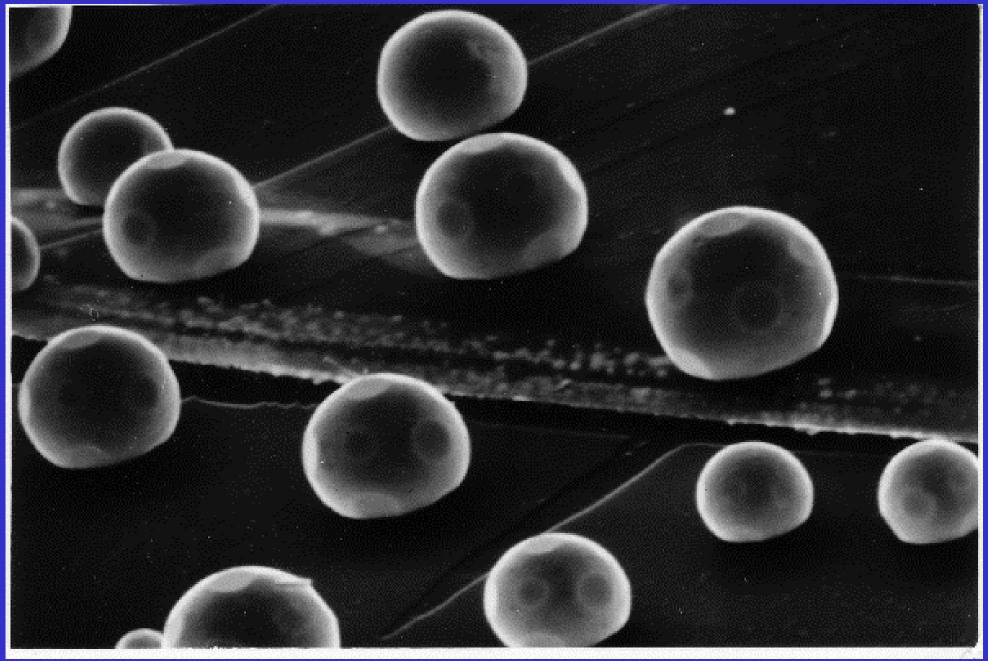
The three type of surfaces:
F: flat,
S: stepped
K: kinked

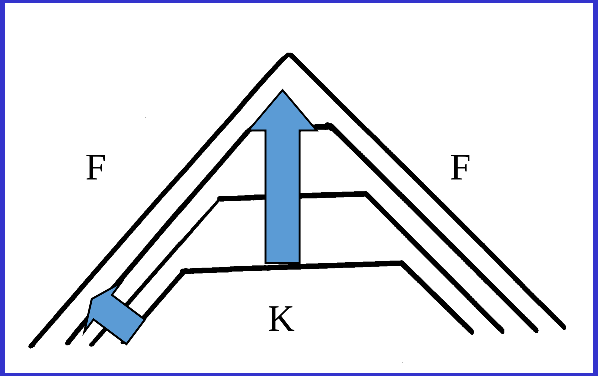


P. L. Ferrari, M. Prähofer, and H. Spohn,
Phys. Rev. E 69, page 035102, ***2004.***

Growth shapes versus equilibrium shape

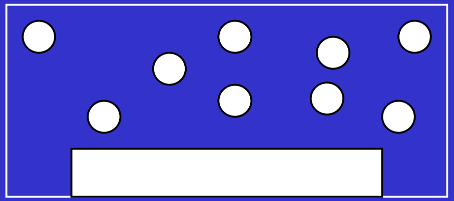






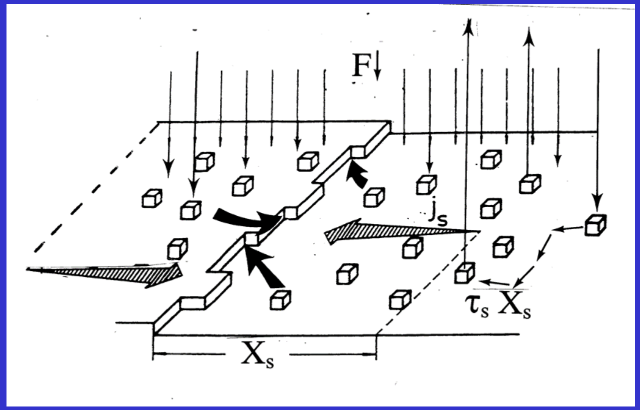
F. Frank, in Growth and perfections of crystals, John Wiley and sons, New York (1958), 411

K face: Ideal growth by direct incorporation

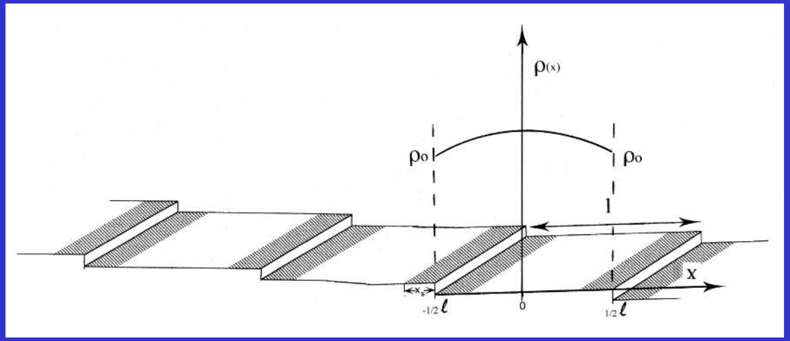


$$V = a^3 \frac{P - P_{eq}}{\sqrt{2\pi mkT}} = a^3 J_{eq}\left[e^{\Delta\mu/kT} - 1\right] \approx K \frac{\Delta\mu}{kT}$$

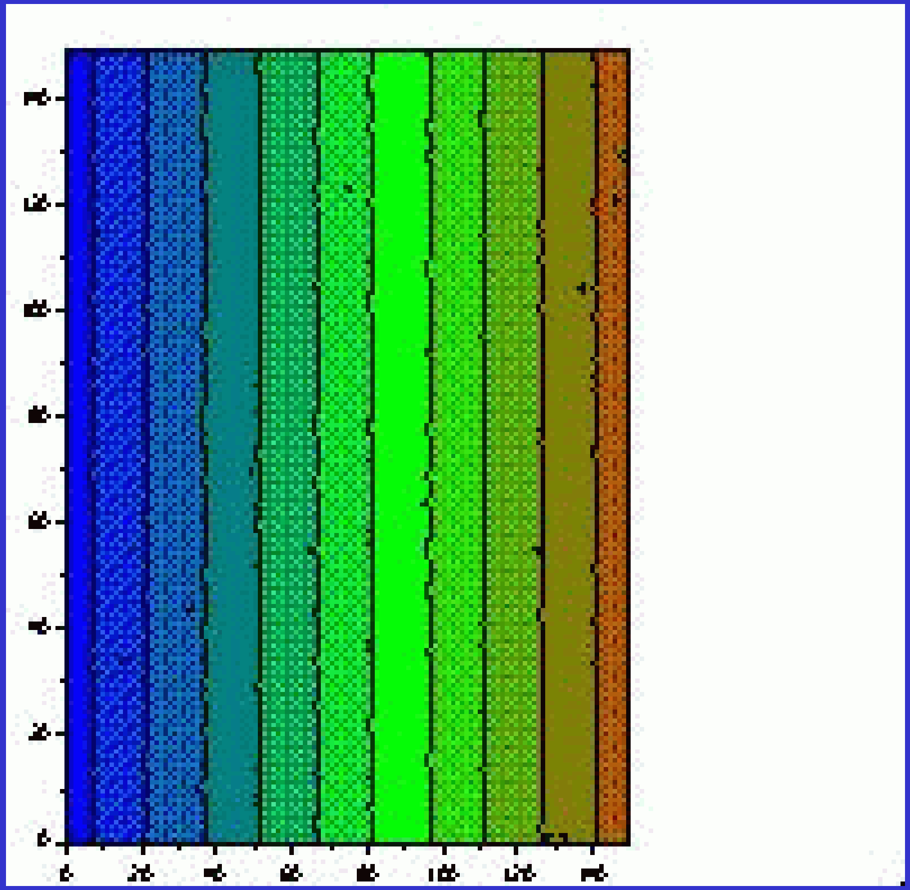
S face: Ideal Vicinal growth by step flow



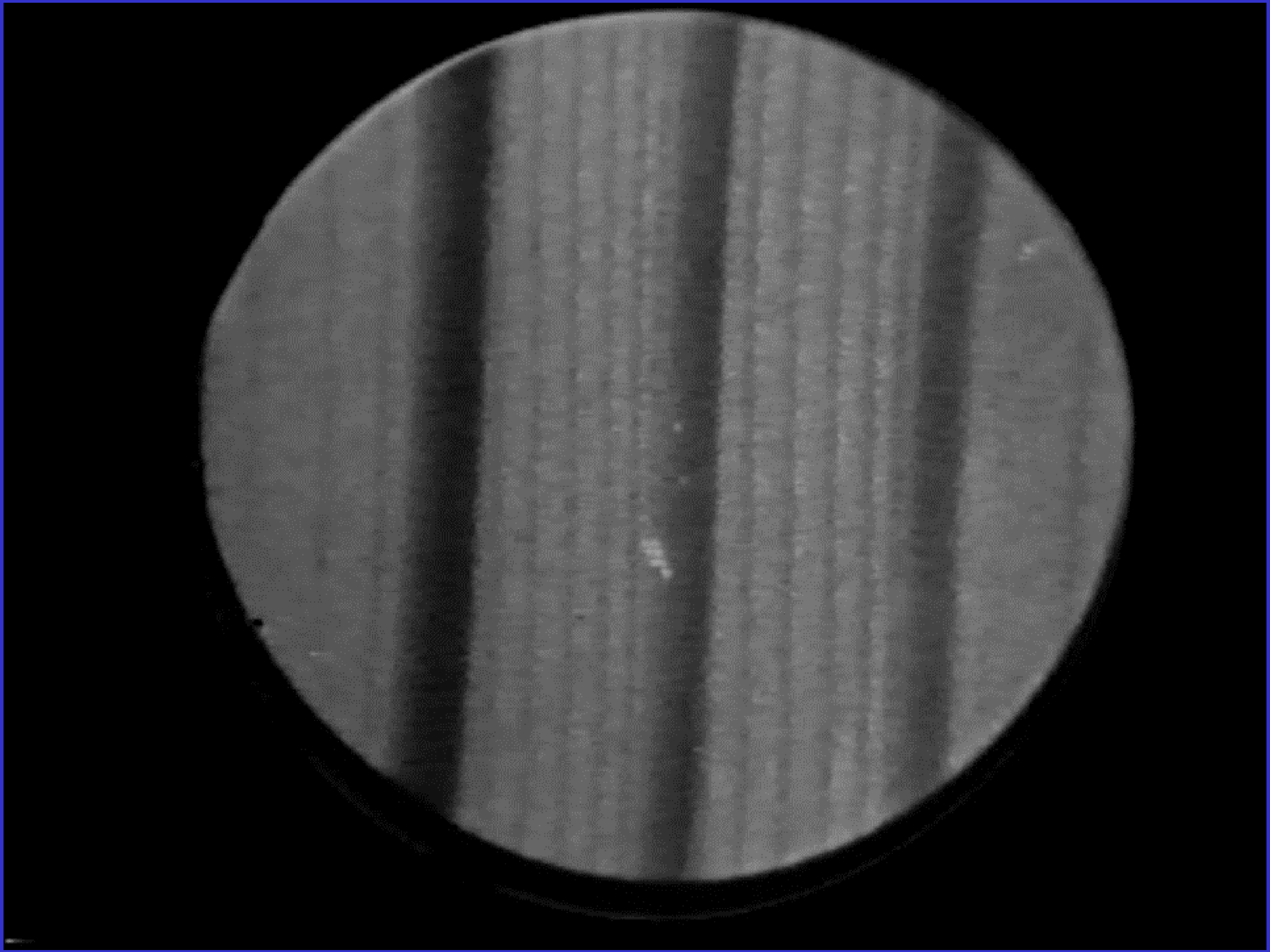
$$D_s \frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau_s} + J = 0$$



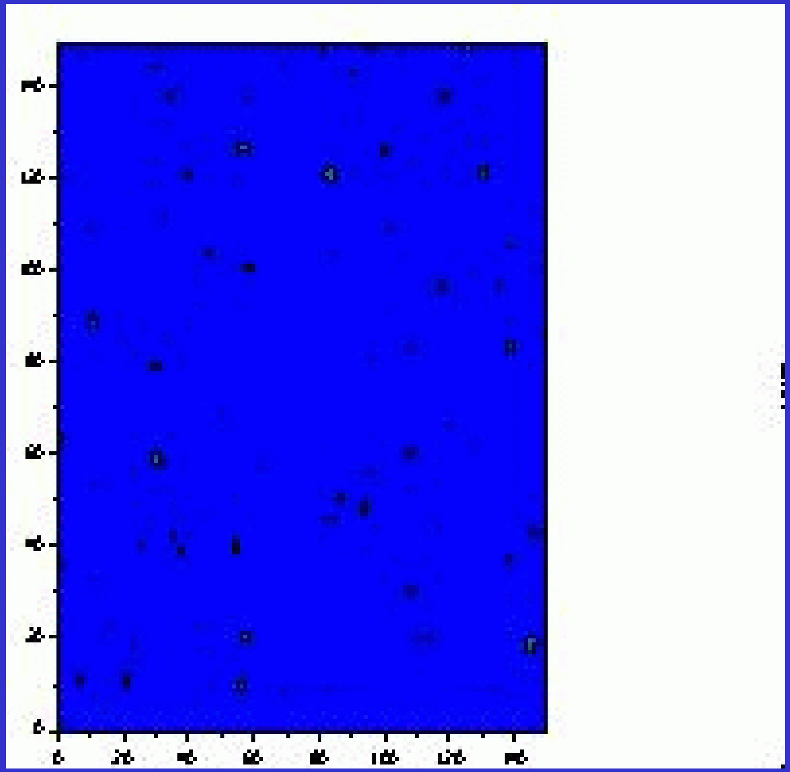
W.K. Burton, N. Cabrera, F.C. Frank, Philos. Trans. R. Soc. Lond. 243 (1951) 299.

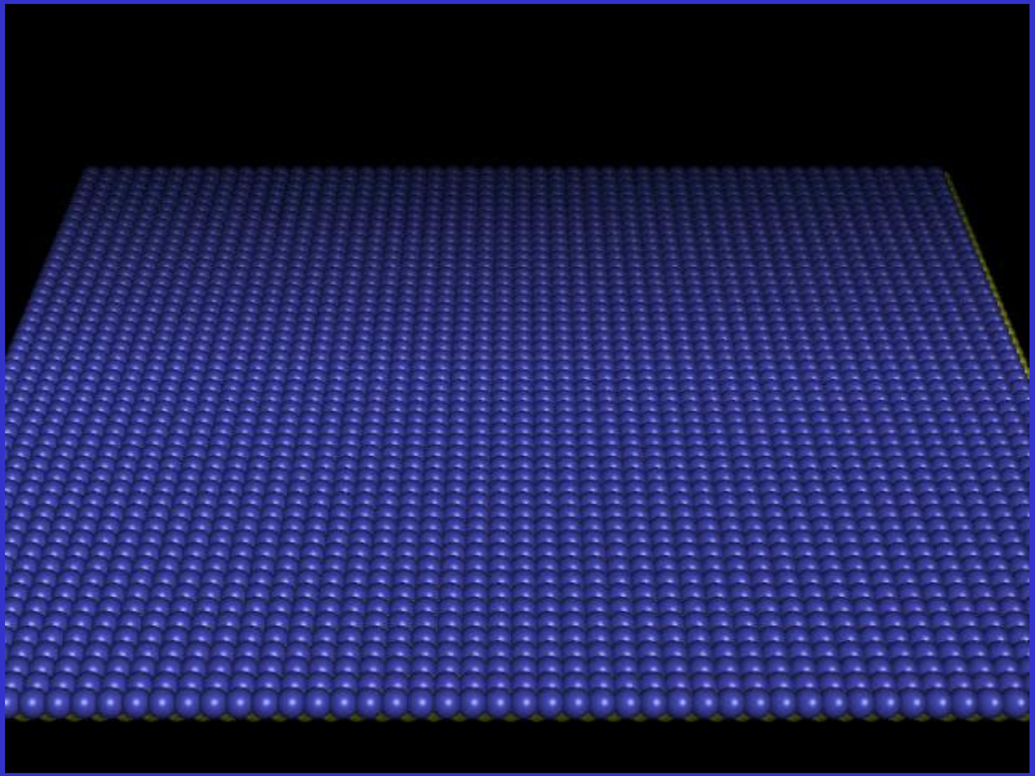


REM movie of step flow on various vicinalities

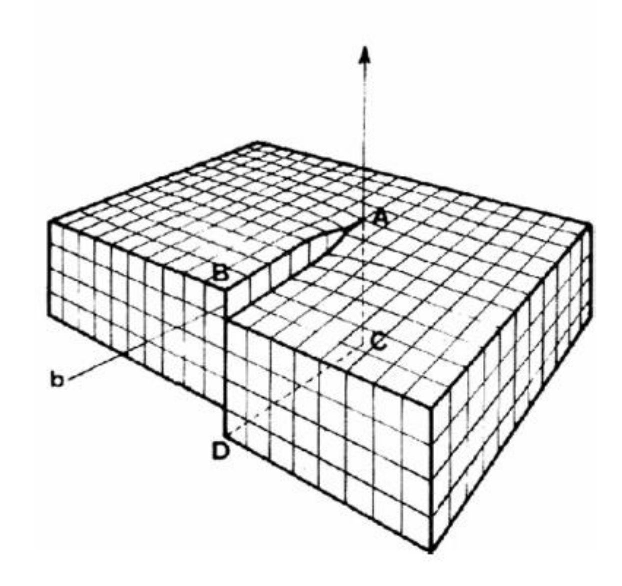


Simulation of the growth on an ideal F face: 2D islands growth

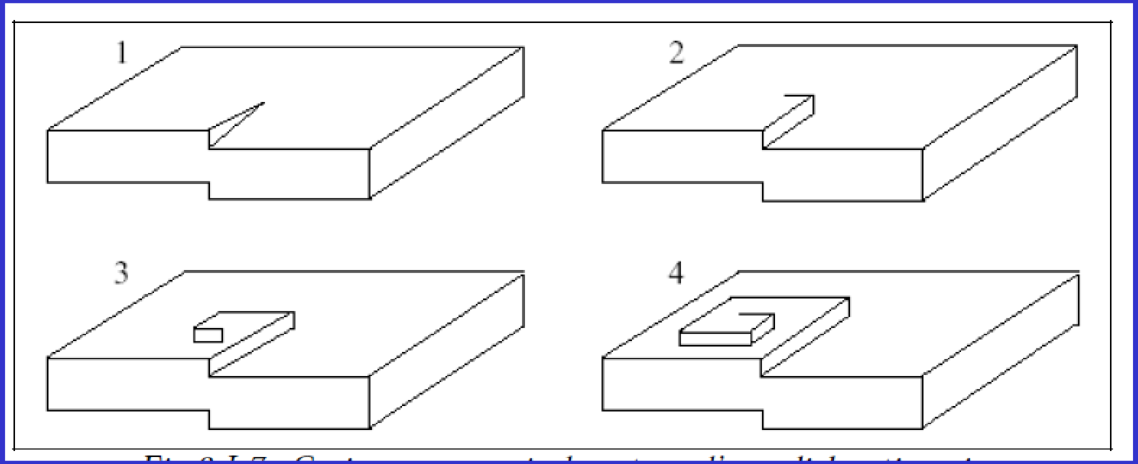




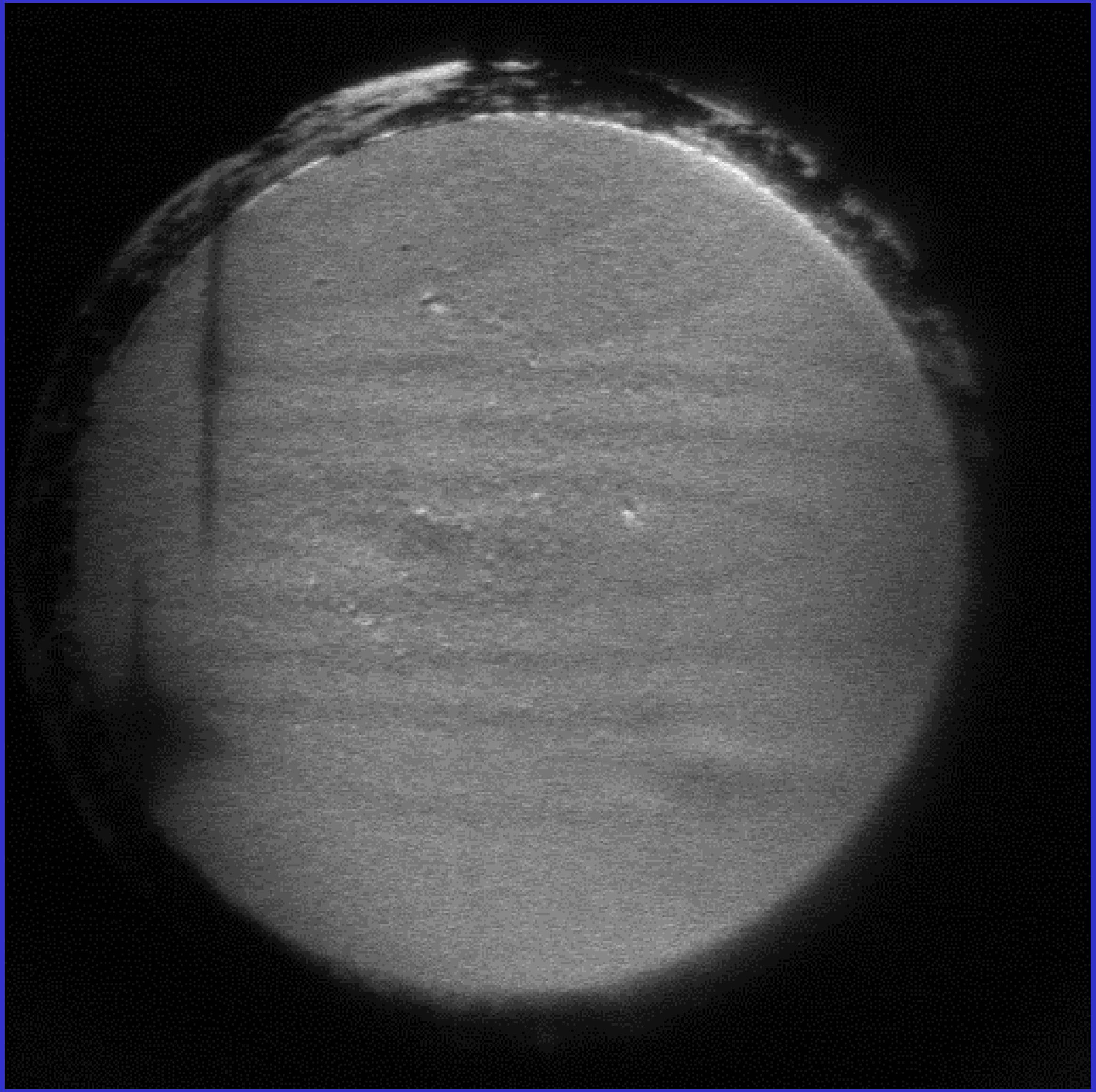
Growth on a Real F face: Pyramidal growth



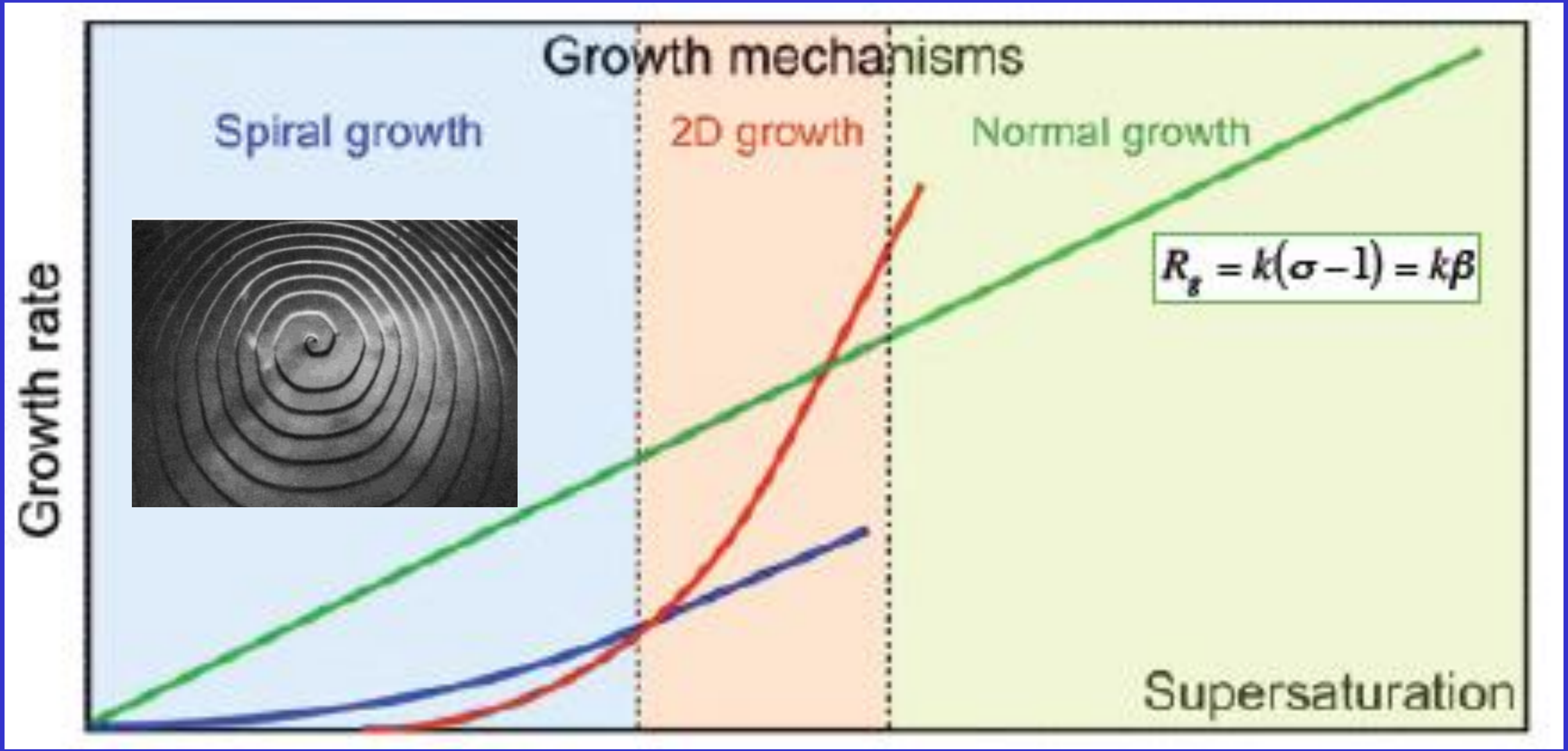
W.K. Burton, N. Cabrera, F.C. Frank, Philos. Trans. R. Soc. Lond. 243 (1951) 299.



LEEM movie of pyramidal growth



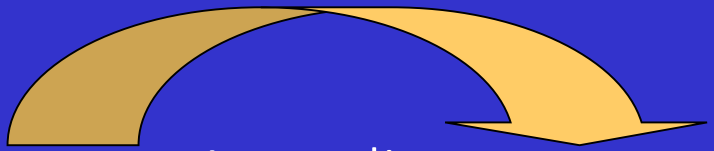
B. Ranguelov et al. Surf. Sci. 600 (2006) 4848


Growth mechanisms
Spiral growth
2D growth
Normal growth
$R_g = k(\sigma - 1) = k\beta$
Growth rate
Supersaturation

V/ Dewetting

Dewetting of a metastable film

Initial state

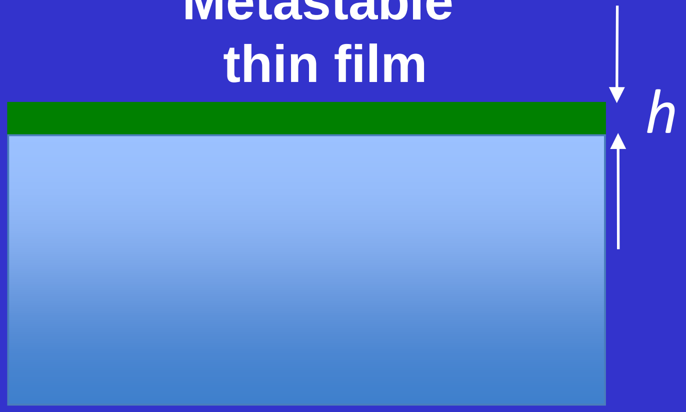


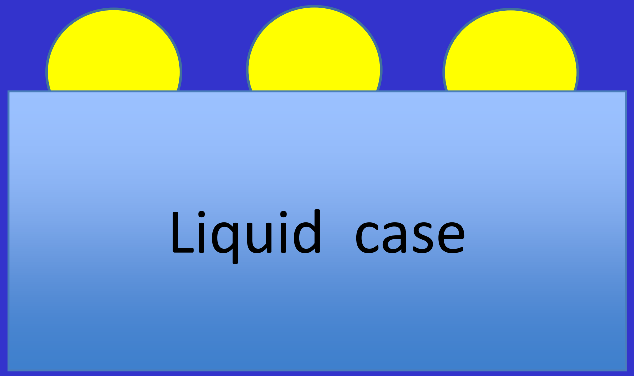
Annealing

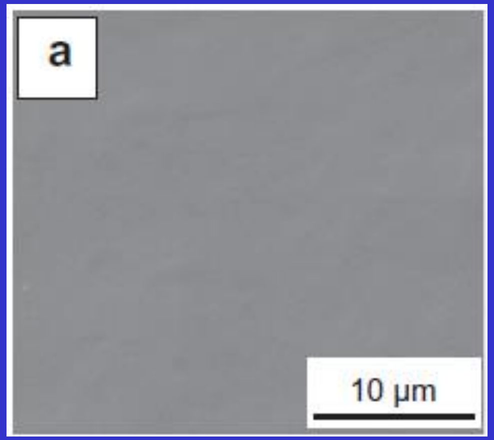
Final state $(\Phi > 0)$

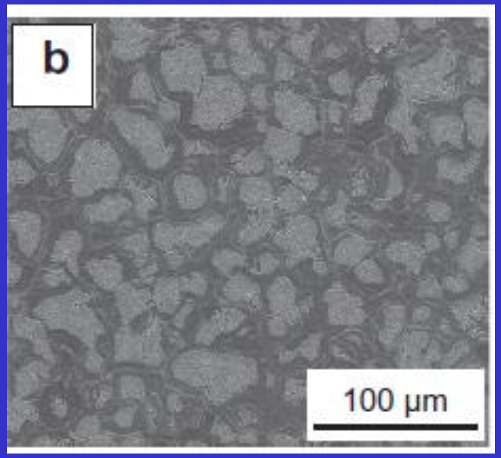
Equilibrium situation

Metastable thin film





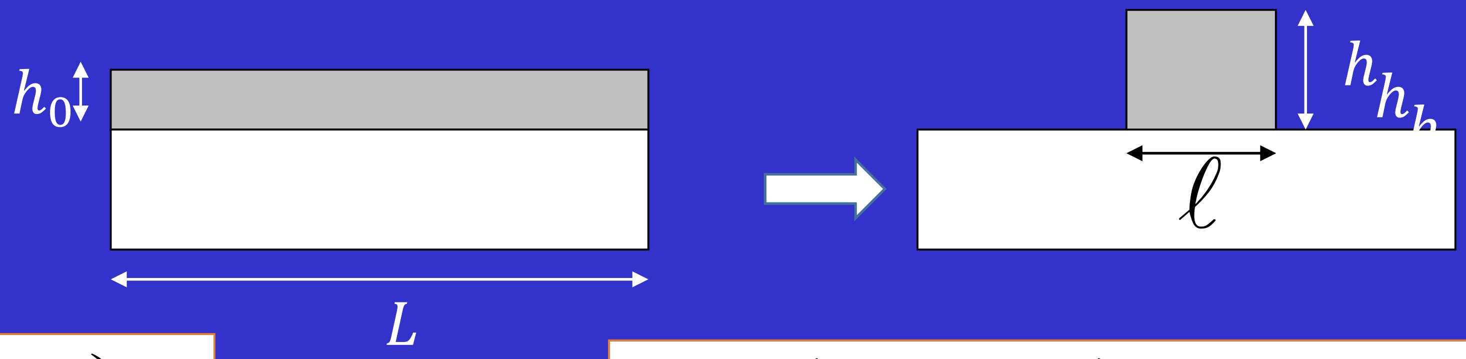




Pt/Cr

Hanief Nucl. Inst. Meth (2015)

Dewetting of A/B: The essential



$$F_i = \left(\gamma_A + \gamma_{AB}\right) L^2$$

$$F_f = \left(\gamma_A + \gamma_{AB}\right)\ell^2 + \gamma_B\left(L^2 - \ell^2\right) + 4\gamma_A' h\ell$$

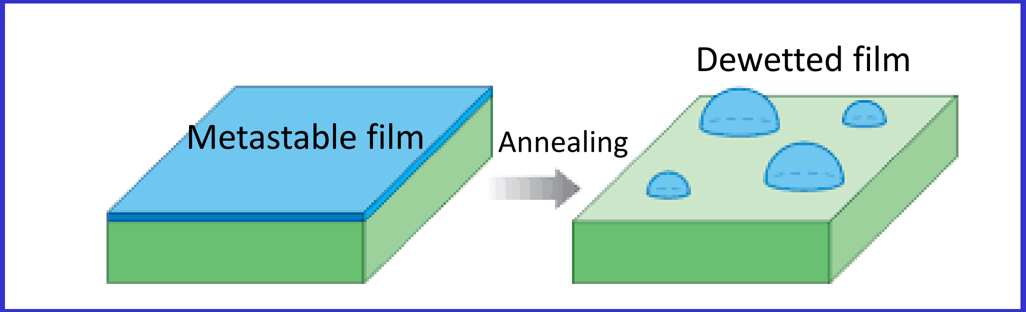
Surface energy change :

$$\Delta F = \left(\gamma_A + \gamma_{AB} - \gamma_B\right)\left(\ell^2 - L^2\right) + 4\gamma_A' h\ell$$

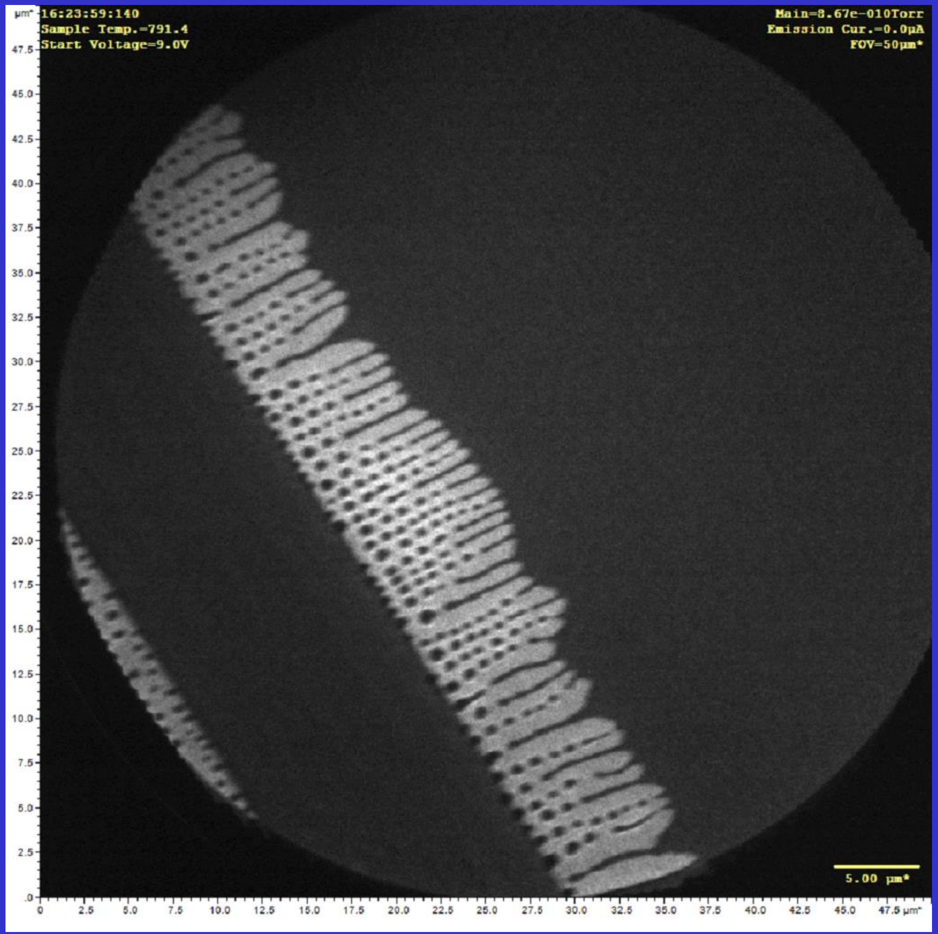
Wetting for negative ϕ

Dewetting for positive ϕ

Example :
Dewetting of SOI

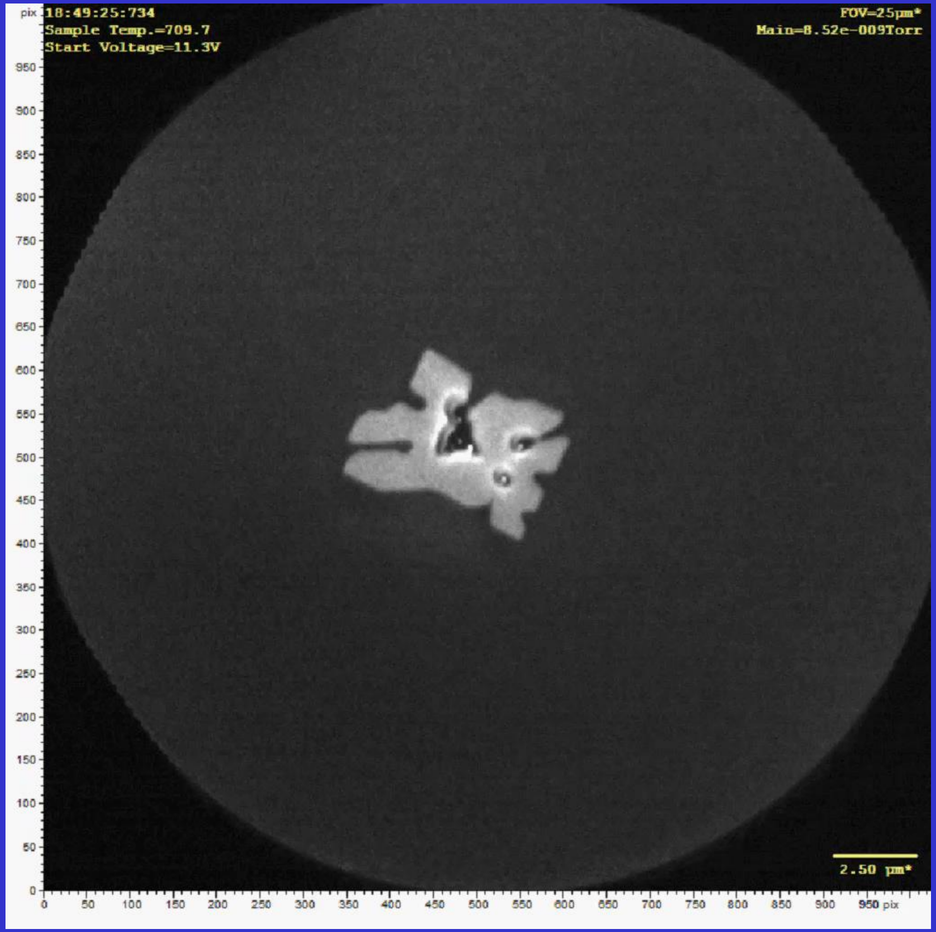


LEEM movie of dewetting from a front

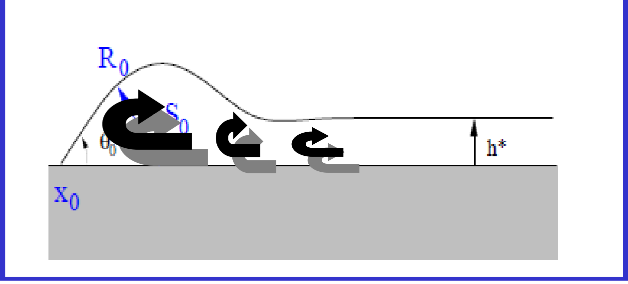
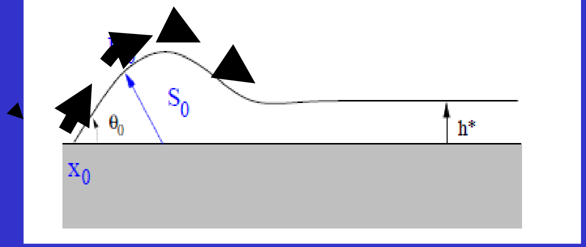


E. Bussmann et al.
New J. Phys. 13 (2011) 043017

LEEM movie of dewetting from a hole



Dewetting: liquids versus solids

	Liquids	Solids
Mechanisms	Hydrodynamics, mass motion 	Surface diffusion 
Structure	Isotropic	Anisotropic
Theoretical concepts	Surface tension	Surface free energy and Surface stress

Continuous models for solids or liquids (Mullins approach based on surface diffusion)

$$\frac{dh}{dt} = -\vec{\nabla}.\vec{j}$$

Mass conservation

$$\vec{j} = -\vec{\nabla}\,\mu$$

Transport: surface diffusion

$$\mu \sim \kappa$$

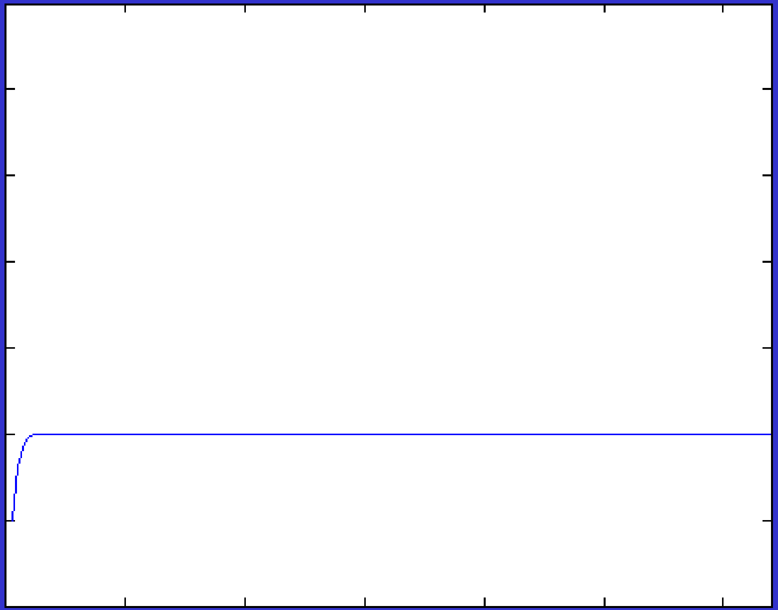
Driving force: curvature

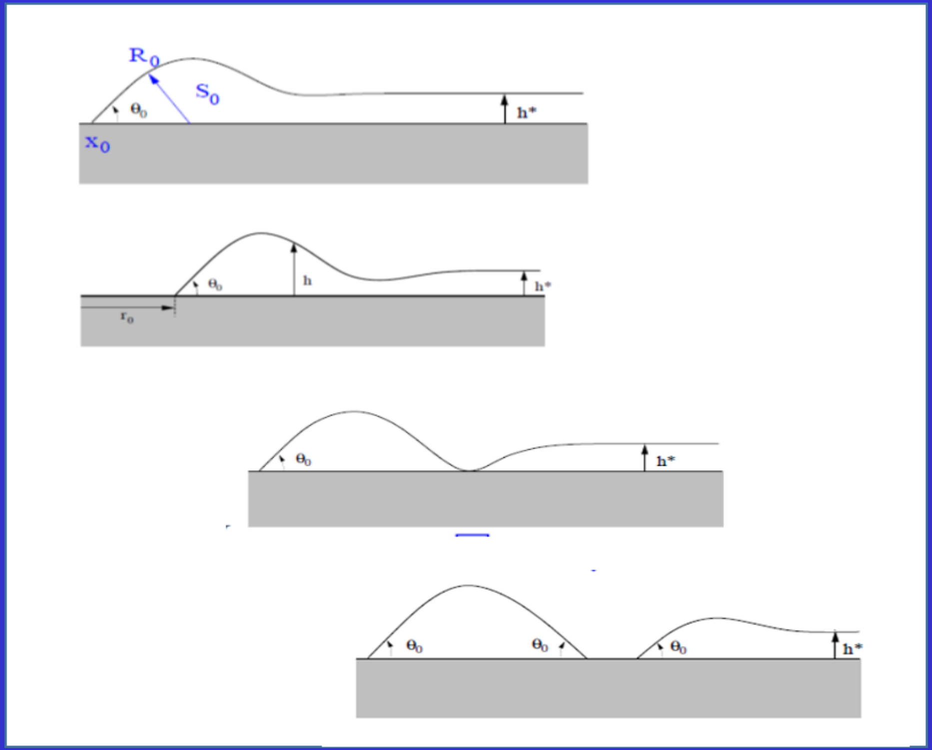
Mullins Equation

$$\frac{\partial h}{\partial t} = -B h_{xxxx}$$

$$B = \frac{D_s \nu \gamma \Omega^2}{kT}$$

Receding of a straight front: simulation



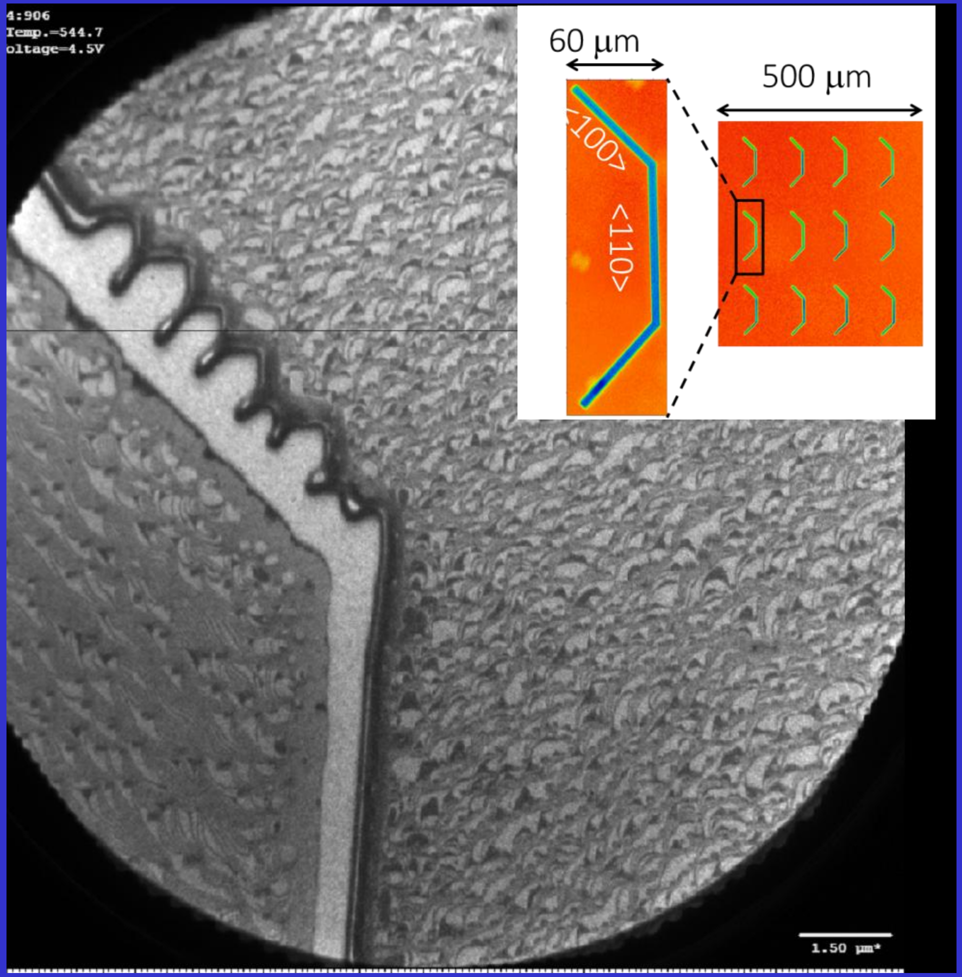


Mullins, JAP 28 (1957) 333

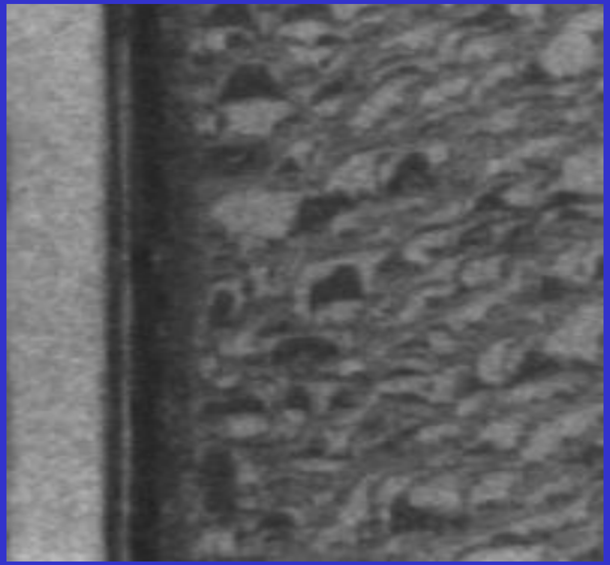
F. Cheynis et al. CR Phys. 14 (2013)

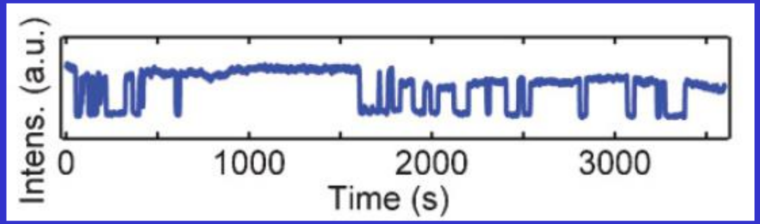
$x(t) \sim t^{2/5}$ $h(t) \sim t^{1/5}$

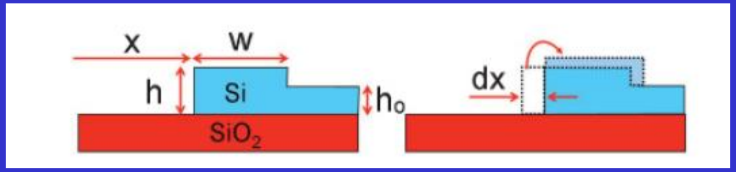
Anisotropy effects



LEEM movie of front thickening

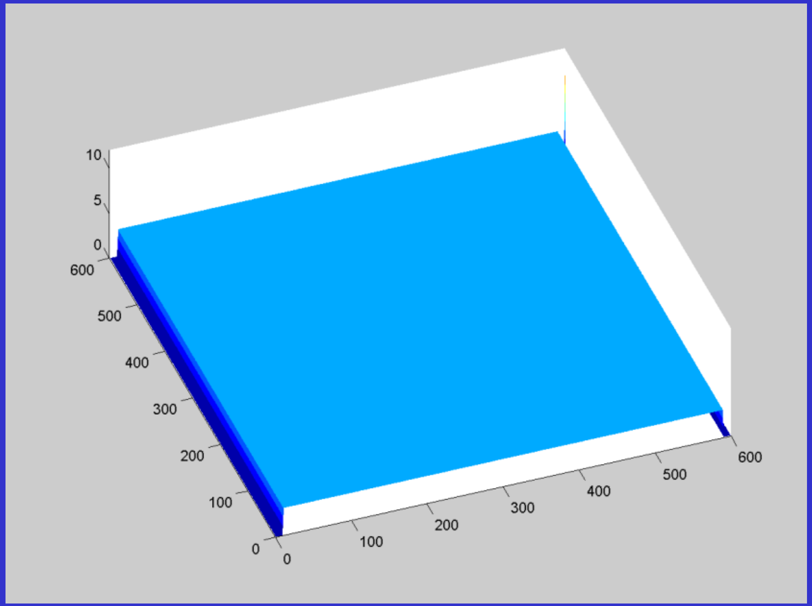


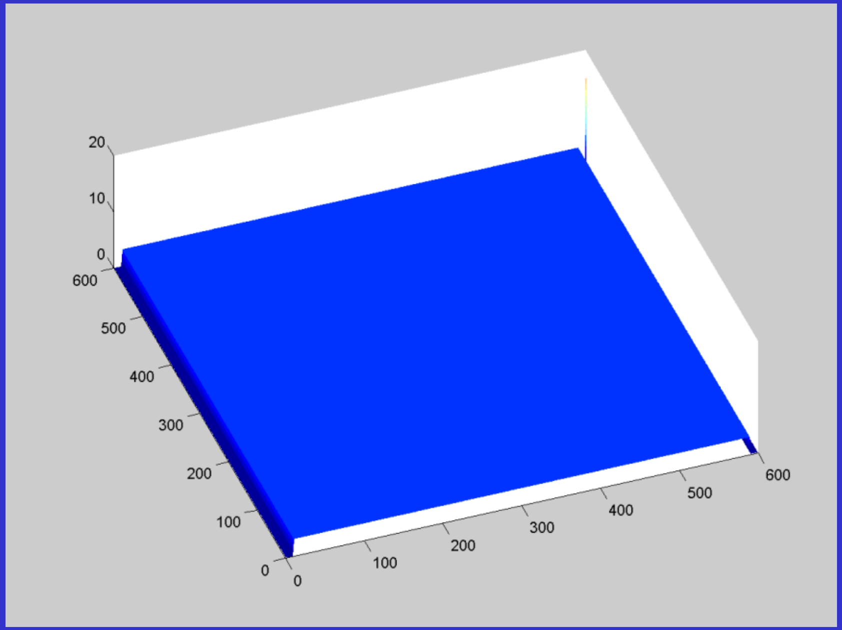


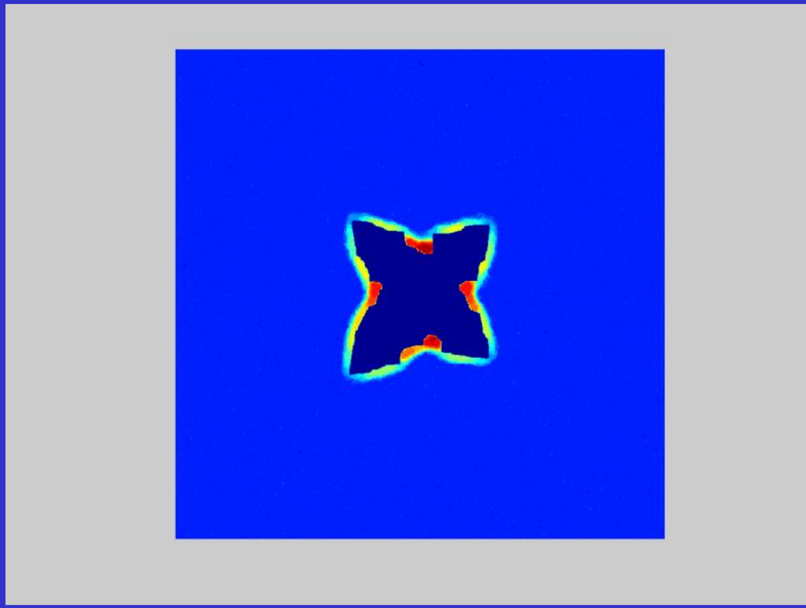


F. Leroy et al.
PRB 85 (2012)n195414

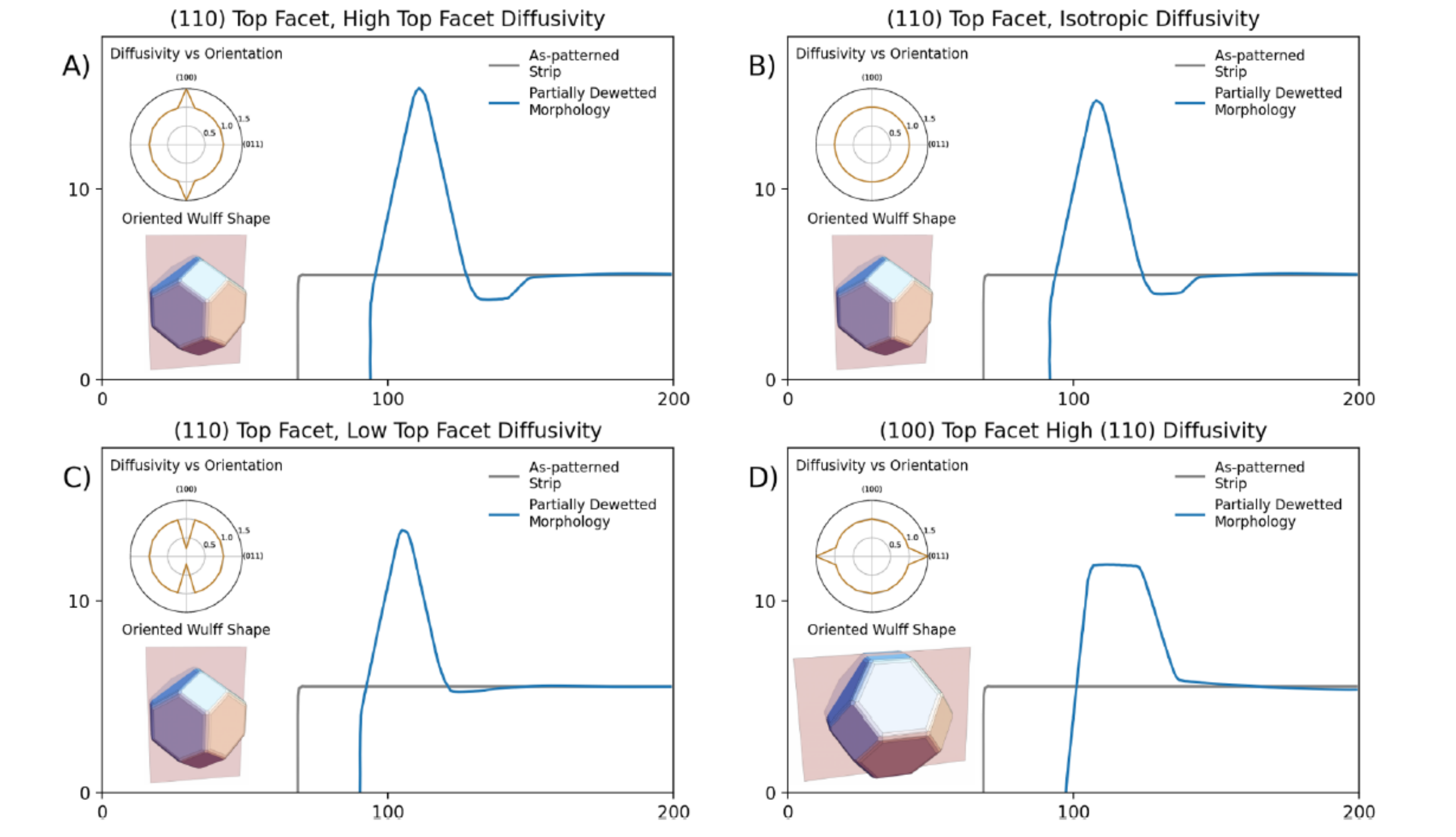
KMC Simulations

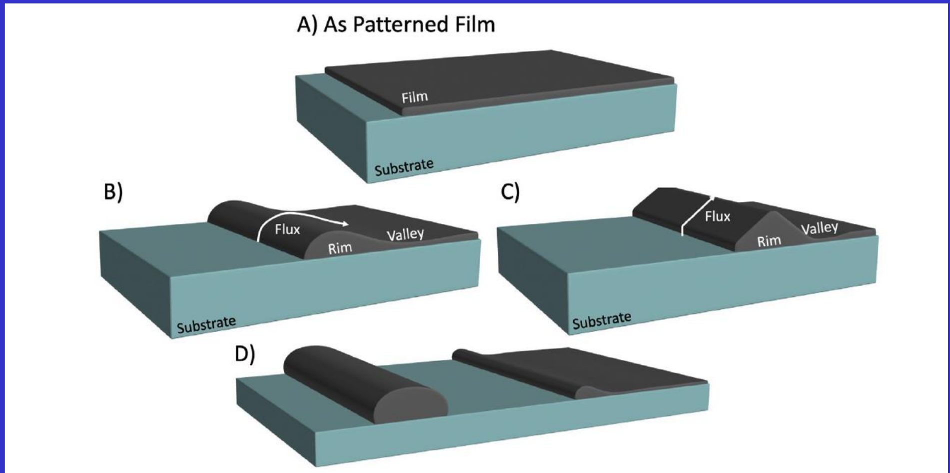


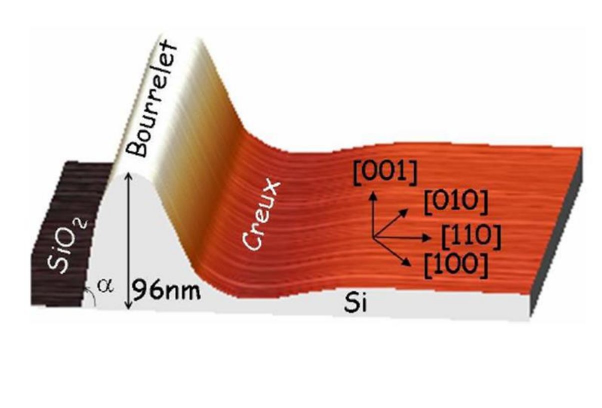




PhD thesis T. Passanante 2014







L'Etoile et al. Acta Mat. 282 (2025) 120368

Dornel et al. PRB 73 (2006) 115427

Continuous models for solids or liquids (Mullins approach based on surface diffusion)

$$\frac{dh}{dt} = -\vec{\nabla}.\vec{j}$$

Mass conservation

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Transport: surface diffusion

$$\mu \sim \kappa$$

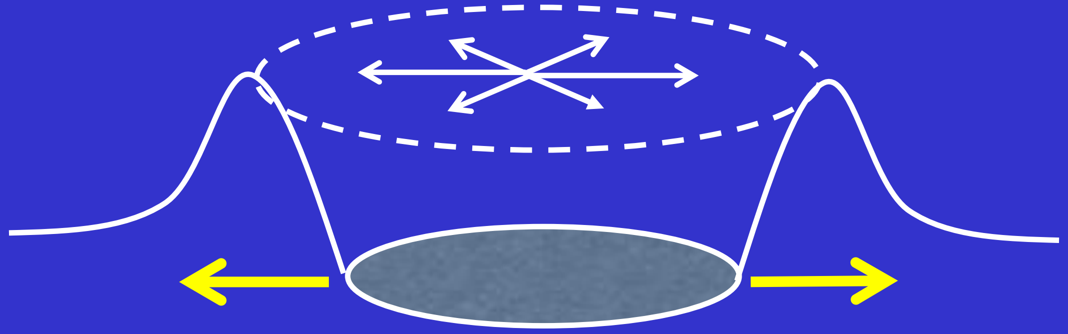
Driving force: curvature

Mullins Equation

$$\frac{\partial h}{\partial t} = -B h_{xxxx}$$

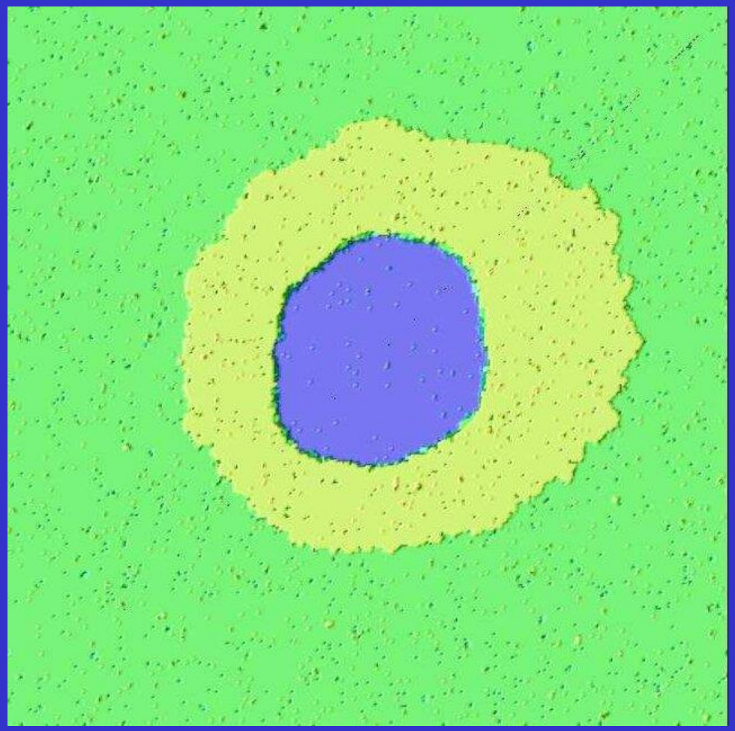
$$B = \frac{D_s \nu \gamma \Omega^2}{kT}$$

Opening of a circular hole:



$R(t) \sim t^{1/4}$

D.J. Srolovitz and C.V. Thompson Thin Solid Films (1986)

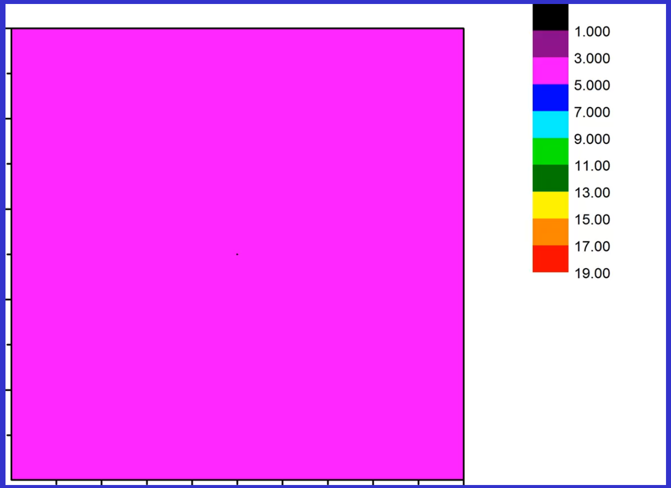


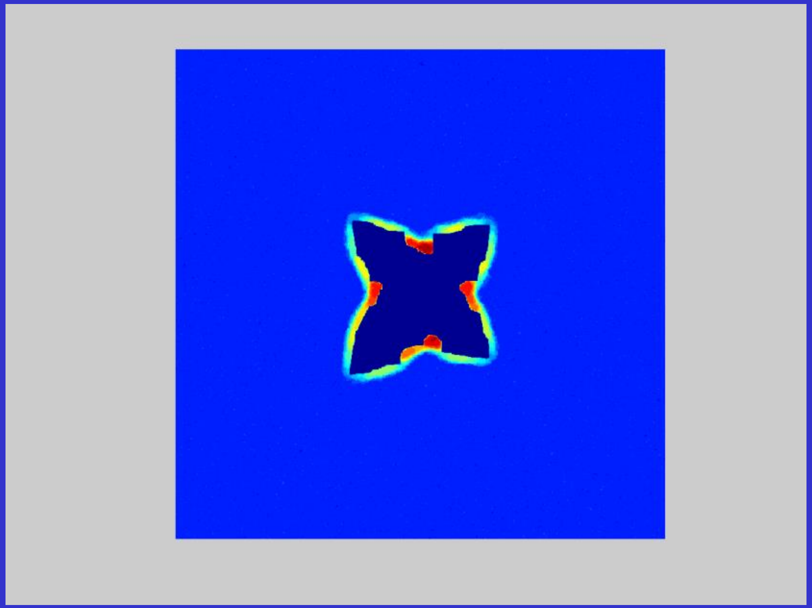
O. Pierre-Louis et al. PRL 99 (2007); PRL 103 (2009); PRB 90 (2014)

F. Cheynis et al.   PRB 84 (2011) 245439

Dewetting from a hole in a Si(001) film

KMC simulation



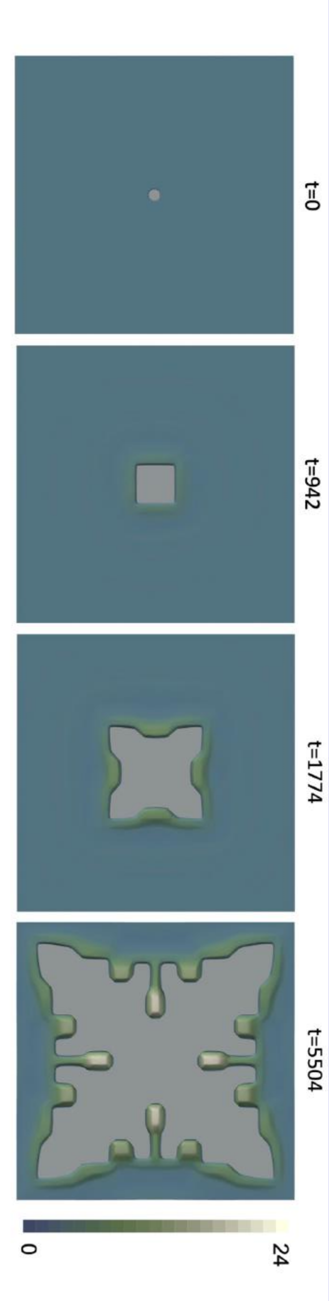


Hole

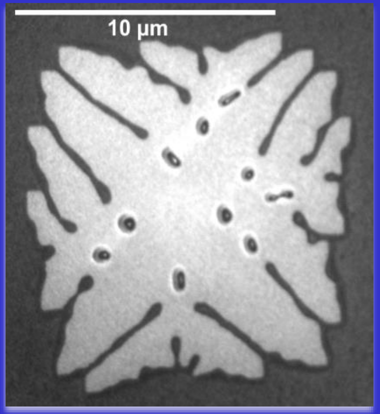
Wulff shape

Corner instability

Island formation

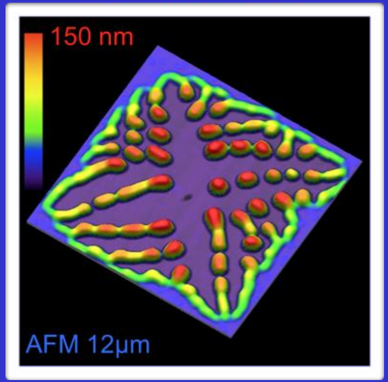


LEEM

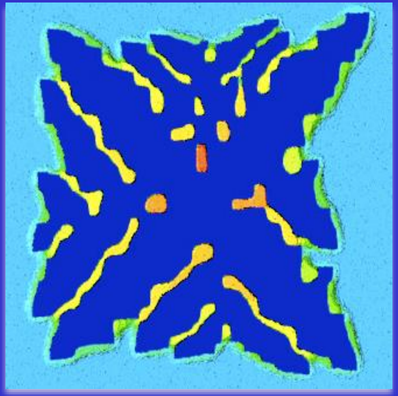


22 nm SOI T~800°C

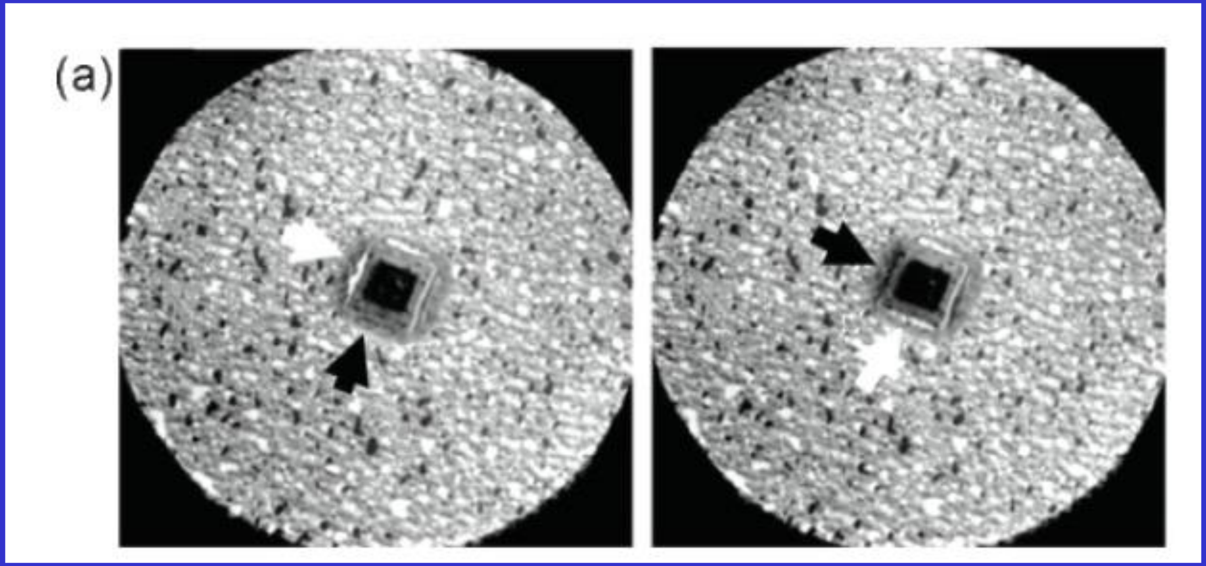
AFM

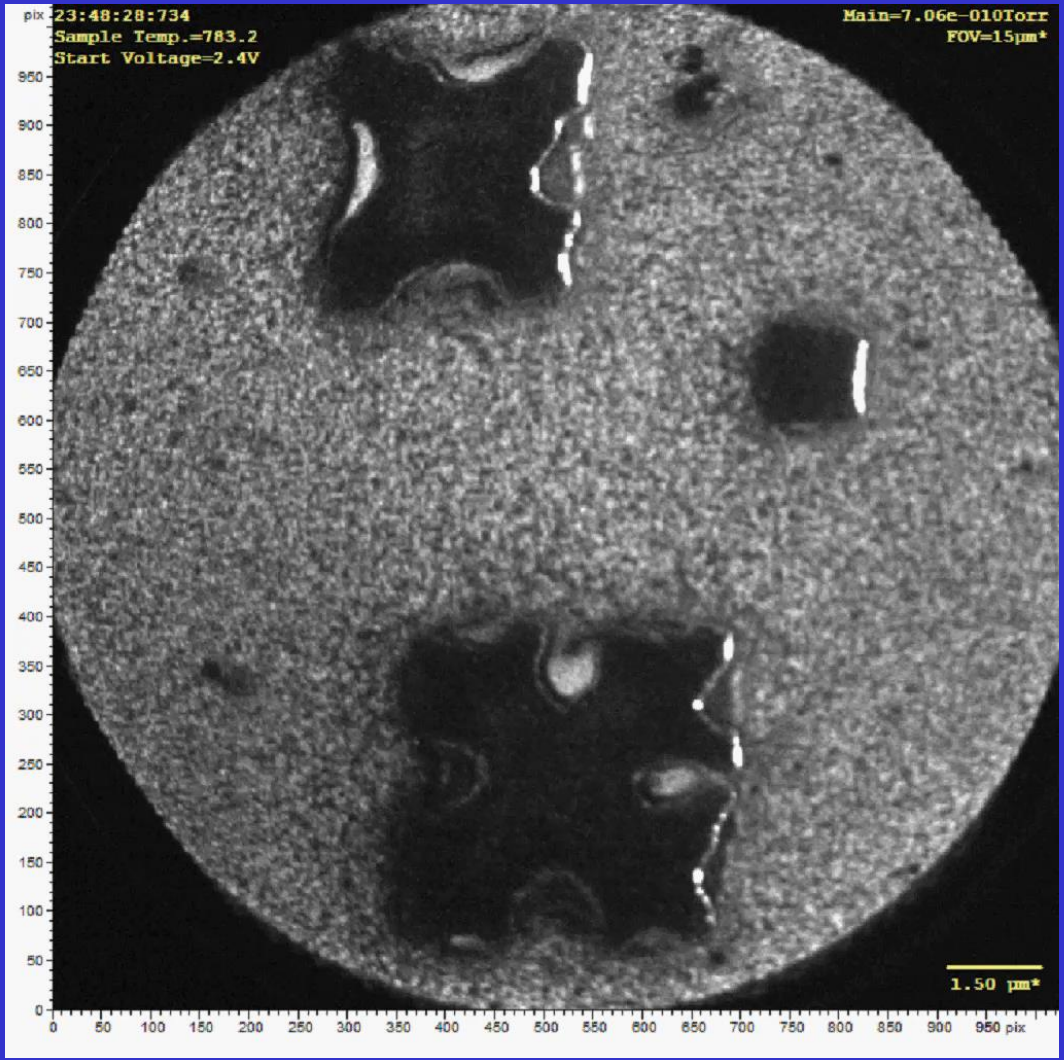


KMC



Dewetting mechanism fom a hole



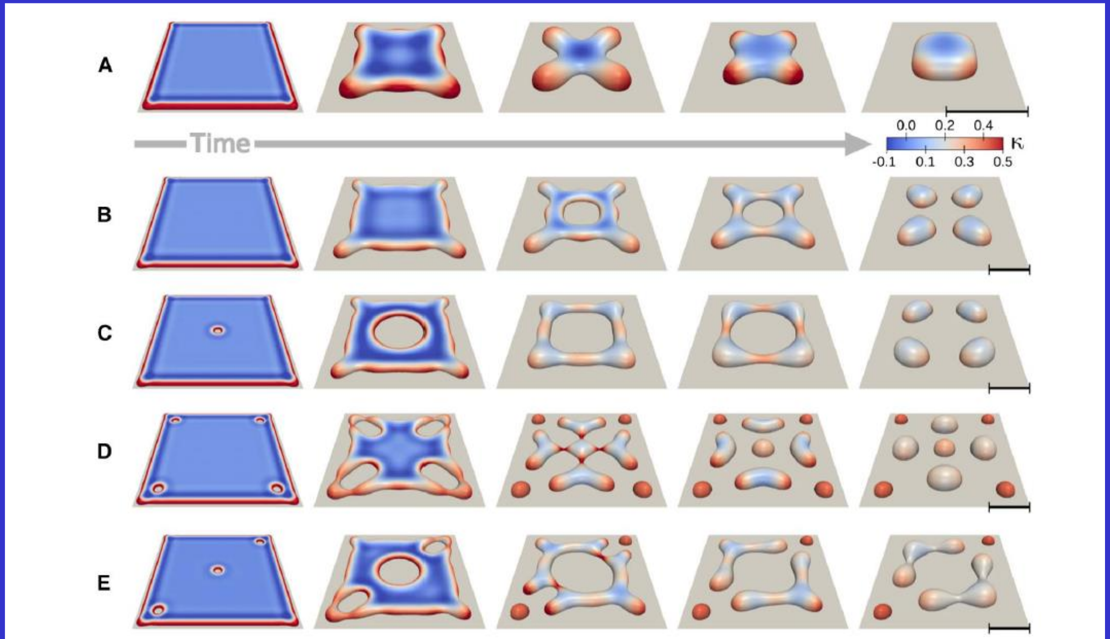


F. Cheynis et al.
PRB 84 (2011) 245439

Can we master the dewetting ?

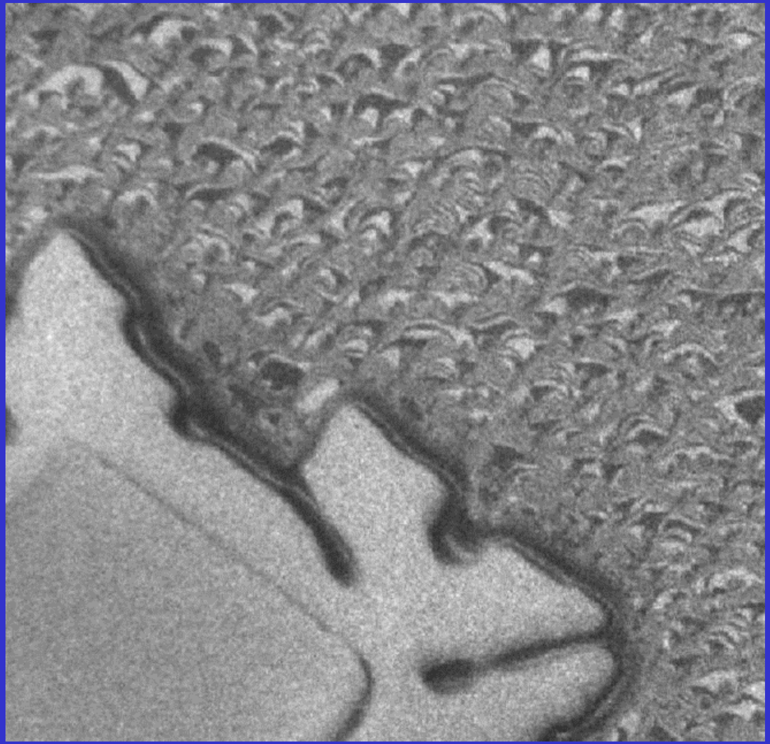
For a review: *F. Leroy et al. surf. Sci. Rep. 71 (2016) 391*

Dewetting from pattern

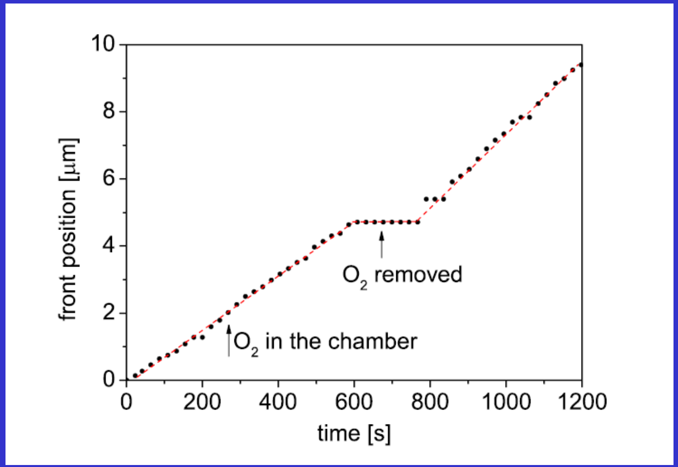


Naffouti et al., Sci. Adv. 2017;3

Dewetting inhibition



S. Curiotto et al.
APL 104 (2014) 061603



Thank for your attention