Elastic instabilities in silicon-germanium films

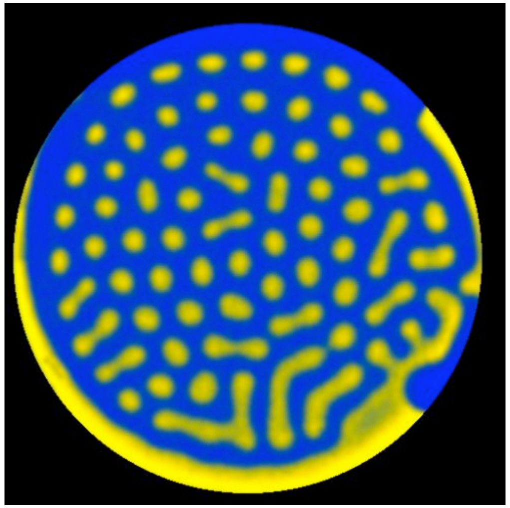
Thomas Frisch, Jean-Noël Aqua
IM2NP, CNRS, Marseille

CSCAMM, College Park
October 25, 2010

Introduction

Pattern forming instabilities are ubiquitous in non-equilibrium dissipative system: three classical examples

Turing Structures



Chemical Turing patterns
Judit Horváth, István Szalai,
Patrick De Kepper, *Science*, 8
Mai 2009.

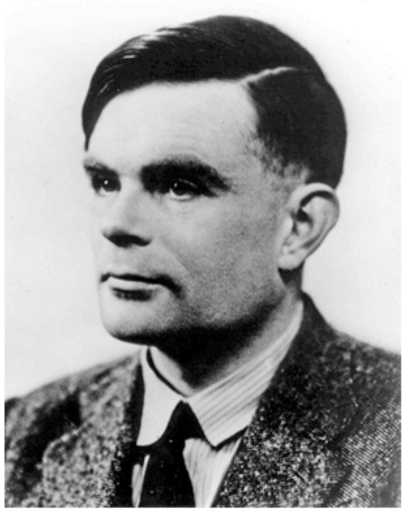
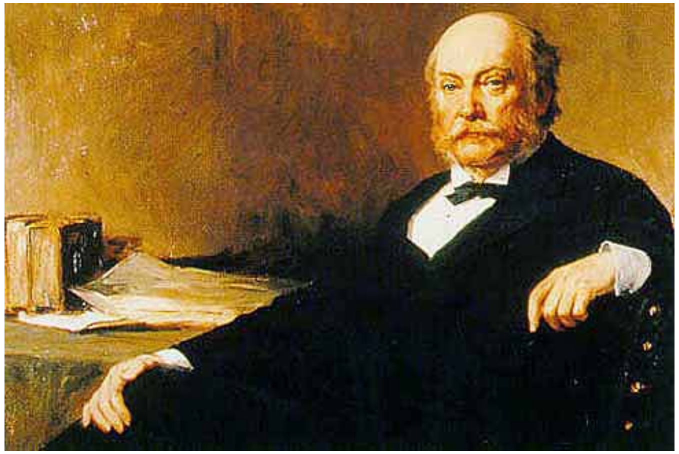


Figure 1. (a) Polymorphism in females of *Papilio dardanus*: (i) *trophonius*, (ii) *cenea*, (iii) *planemoides*, (iv) *hippocoonides*. (b) Male pattern. (Courtesy of Dr A. P. Vogler and Dr A. Cirdak of the Natural History Museum, London, and Imperial College, Silwood Park.)

Alan Turing

Hydrodynamics convection

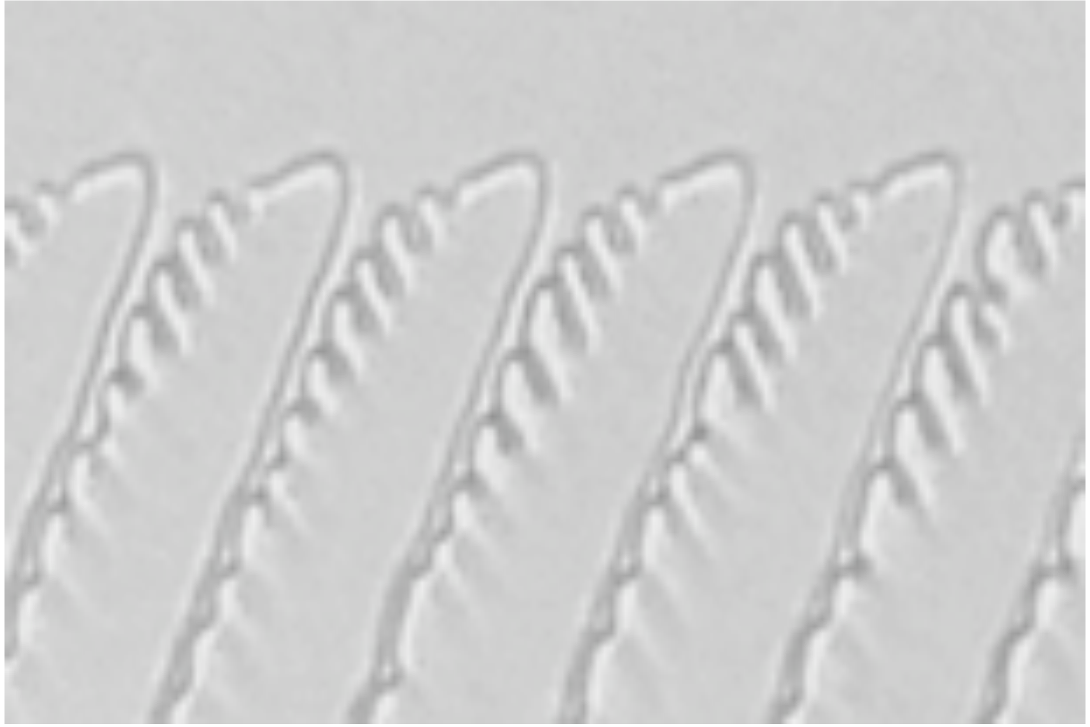


Lord Rayleigh

Bénard

Assenheimer and Steinberg , PRL, 1993

Mullins-Sekerka instability



Dendritic growth, directional solidification,

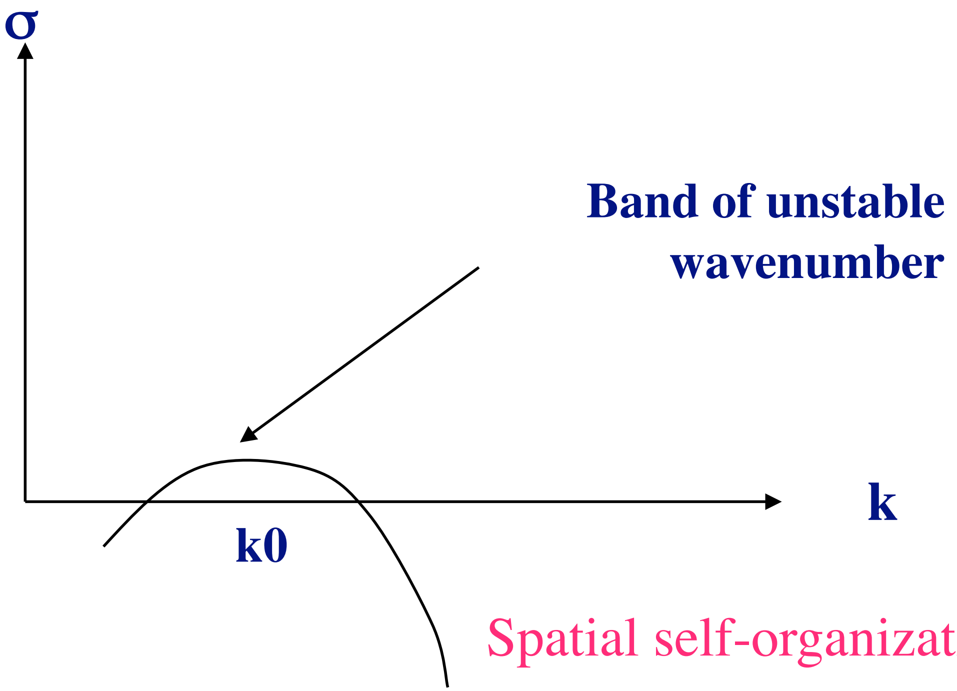
solid-liquid transition, Pocheau

W. Mullins

Common denominator:

- Finite wavelength instabilites, such that there exists a range of unstable wave numbers

Exp (s t) Exp (I k x)

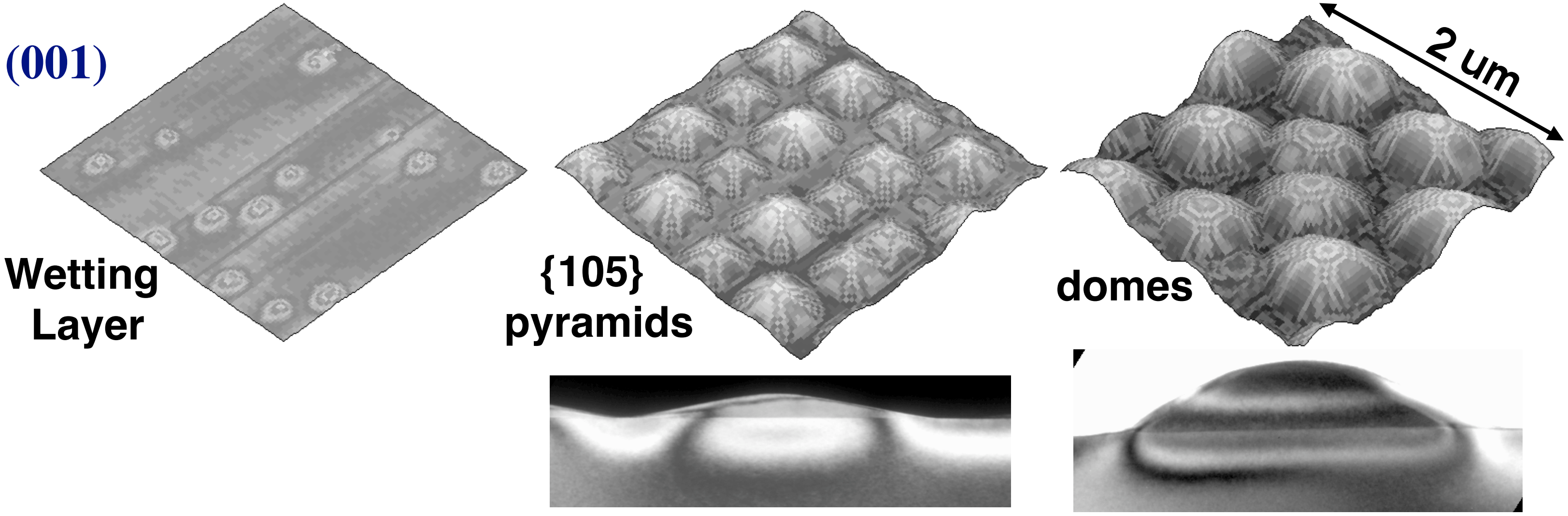


Band of unstable wavenumber

Spatial self-organization

Motivation: Ge_xSi_{1-x}/Si (001) Coherent Islands: instability regime

$Ge_{0.2}Si_{0.8}$/Si (001)
750°C



Floro et al, PRL 79, 3946 (1997)

Spencer, Voorhees, Davis and Mac Fadden, PRL, 1991

Spencer, Voorhees, Davis, PRB, 1993

Spencer, Voorhees, Tersoff, 2001

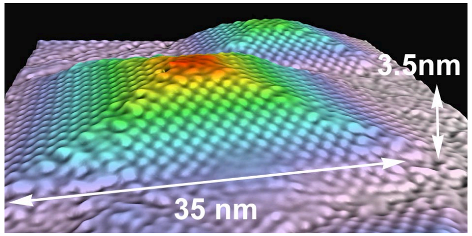
Tromp
Lagally,
PRL 2000

Stangl et al,
RMP, 2004

Ge/Si (001), 600°C

Nucleation regime

G. Medeiros-Ribiero, et al.,
Science 279, 353 (1998).



Questions

- What is the coarsening dynamics?
- What is the influence of the anisotropy of surface energy ?
- What is the influence of the film height?

Outline

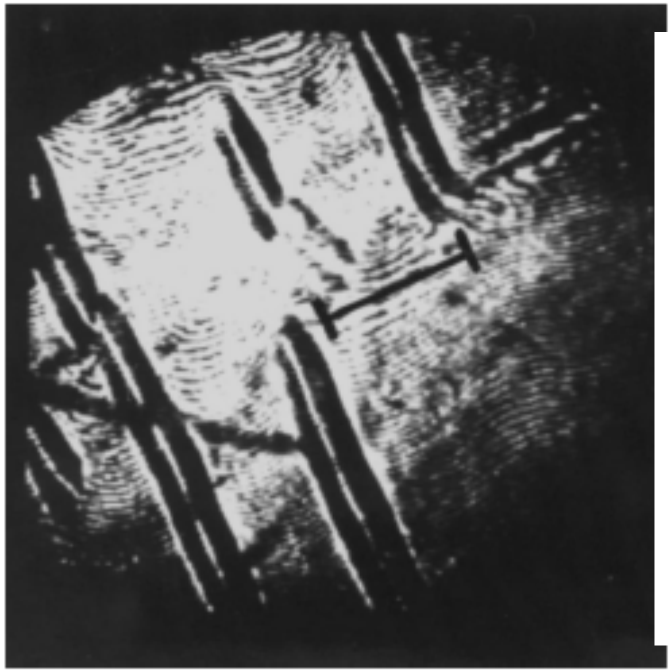
- Asaro-Tiller-Grinfeld Instability

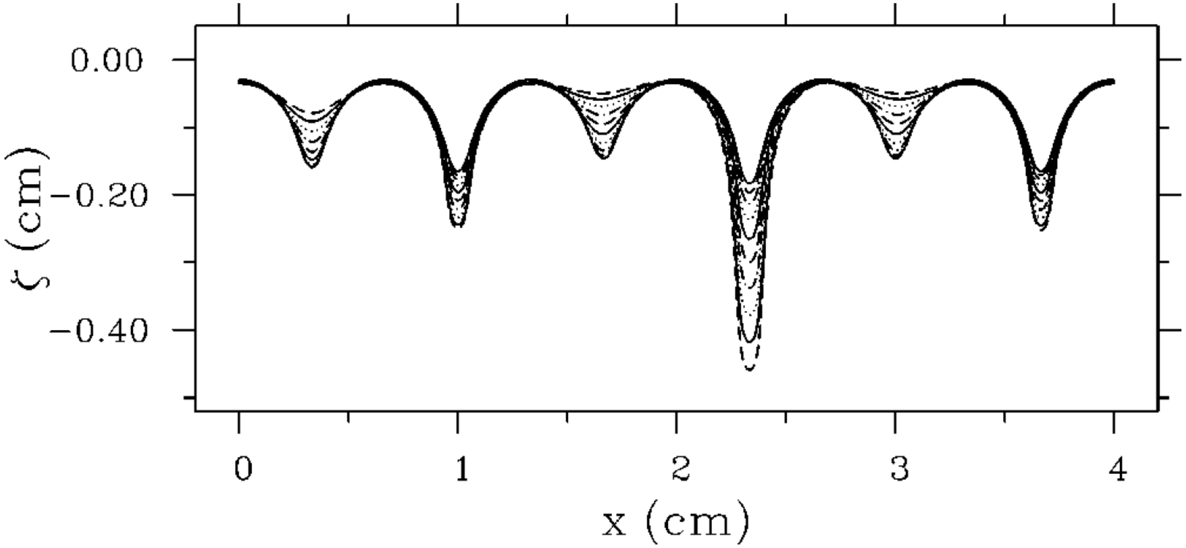
- The Mullins model for hetero-epitaxy

- Isotropic Case (Non interupted Coarsening)
- Anisotropic Case (Interupted Coarsening)

- MBE experiments during annealing
- Conclusion and Perspectives

Grinfeld-instability of liquid-solid helium





Kassner, Misbah et al, 2001, Phys Rev E,

Phase field methods

Bodensohn 1986, Balibar 1991

Balibar 2005 RMP

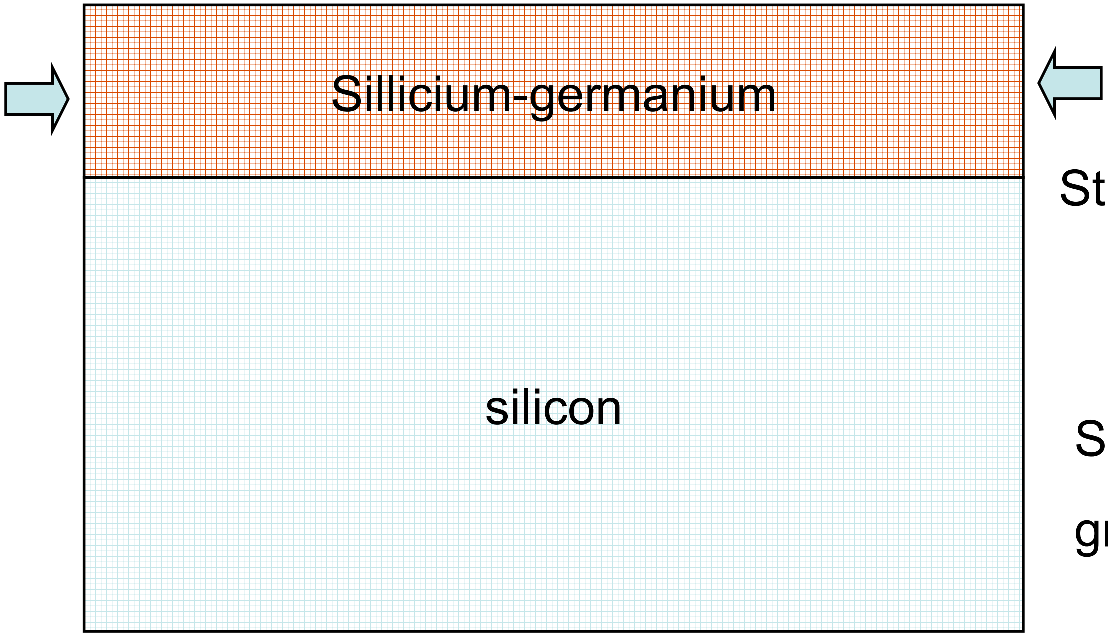
The Asaro-Tiller-Grindfeld Instability: morphological instabilit of a stressed crystal

Germanium atoms are larger then silicon atoms

No cracks or dislocations for small misfit

Film= Si_{1-x} Ge_x

E_f , ν_f



Sillicium-germanium

silicon

Stress due to the misfit

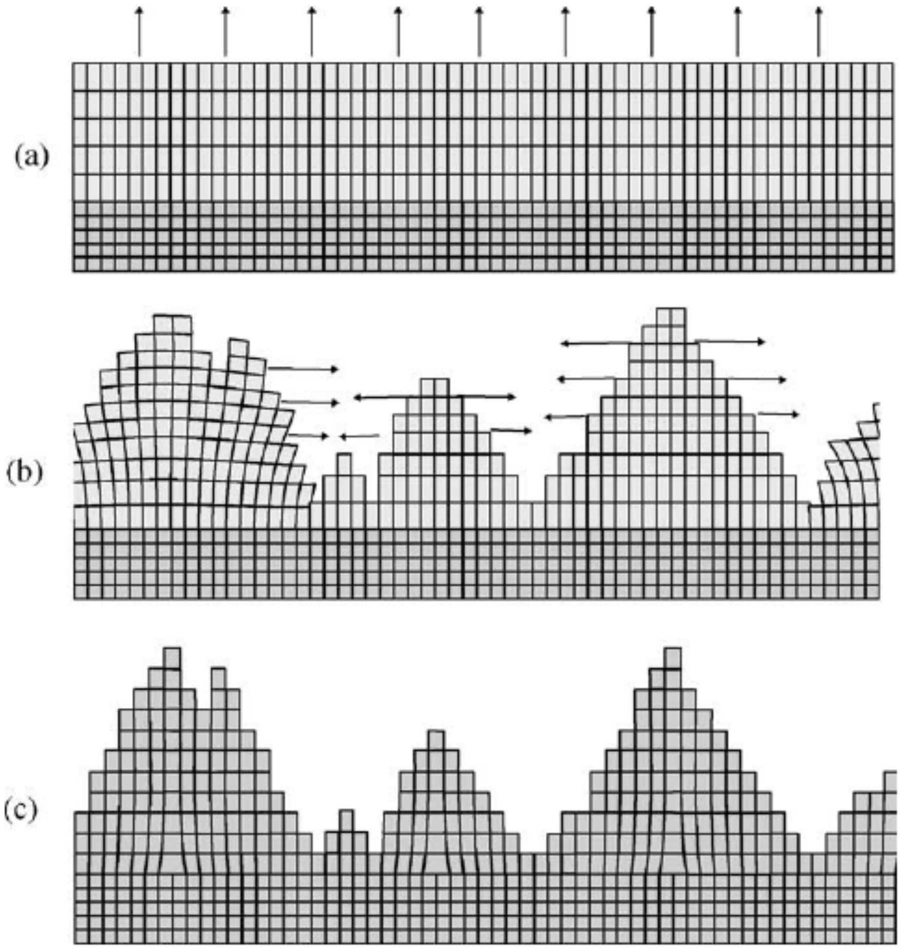
E_s , ν_s

Stranski et Krastanov

growth

MISFIT $\delta a/a$ of the order of 4.2%

Heteroepitaxy : paradigm Si/Ge systems



Stransky-Krastanov mode of growth.
During **annealing**, **islands**, separated by a wetting layer, **form and coarsen**.dominated by surface diffusion

$$a=a_f \;,\; \delta a= a_{film} - a_{substrate}$$

Vegard Law: $a_{film} = x\, a_{ge} + (1-x)\, a_{si}$

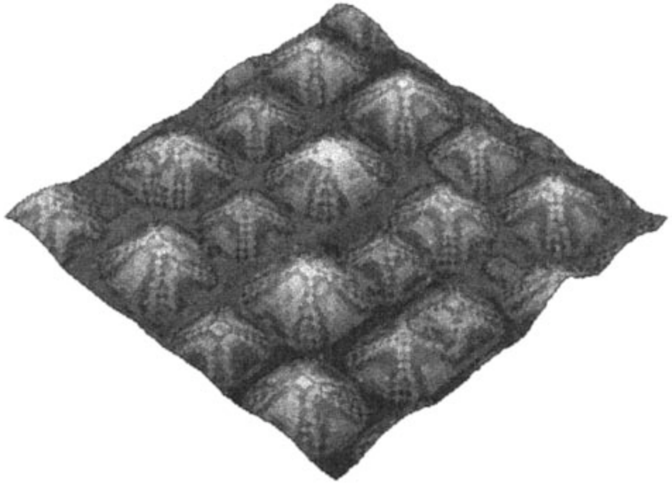
$$l_0 = \frac{\gamma}{E(\frac{\delta a}{a})^2}$$

$$t_0 = l_0^4/(D\gamma)$$

Pimpinelli, Villain « Physics of crystal growth», 1998
Stangl et al, Review of Modern Physics 2004
C. Misbah, O. Pierre-Louis and Y.Saito, Review of Modern Physics, 2010

Heteroepitaxy, Si/Ge (IV/IV) or group III/V InGaAs/GaAs

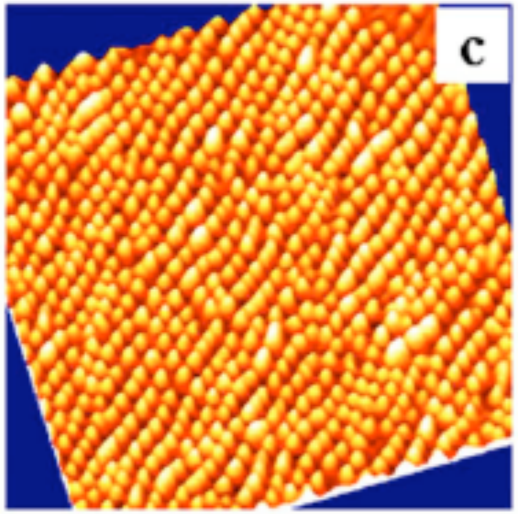
Elastic instability: island formation is ubiquitous



Floro **et al**, PRB 99

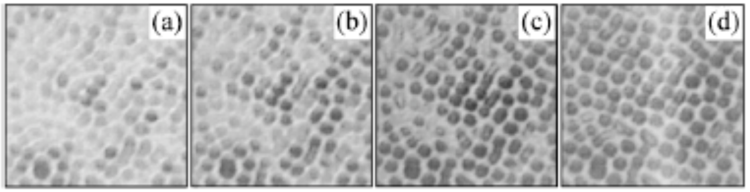
$$l_0^{-1} = \frac{E}{\gamma}\left(\frac{\delta a}{a}\right)^2$$

$$t_0 = l_0^4/(D\gamma)$$



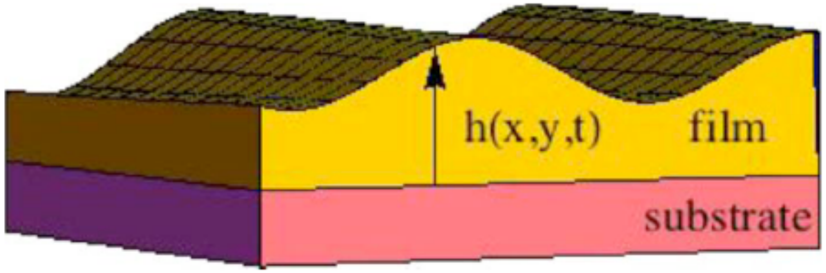
Berbezier, Ronda, PRB 2007, vicinal surface SI (001)

Nucleationless formation of islands in heteroepitaxy from surface ripples.



Sutter et al. PRL 2000

The « Mullins » surface diffusion model



No alloying, no volume diffusion

$$\frac{\partial h}{\partial t} + \nabla \cdot \mathbf{J} = 0$$

$$\mathbf{J} = -D\nabla\mu$$

Elastic energy

Surface energy

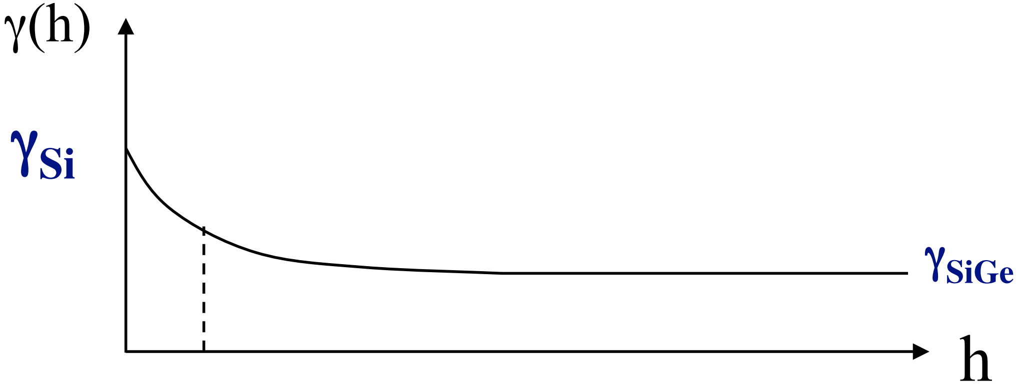
Wetting potential

$$\mu = \mathcal{E}[h] + \gamma(h)\kappa(h) + \gamma'(h)/\sqrt{1+|\nabla h|^2},$$

κ(h) is the curvature

Wetting potential model

$$\gamma(h) = \gamma\left[1 + c_w \exp(-h/\delta)\right]$$



δ is a few layers, ~ 2 nm

Chiu, Gao, 1993,
Muller and Kern,
F. Liu
Spencer, Tekalign, Golovin,
Davis, Voorhess, PRB, 2003
Levine et al, Phys Rev B, 2007
Aqua et al, Phys Rev B, 2007

Film and substrate elasticity

Elastic energy

$$\partial_j \sigma_{ij}^{\alpha} = 0$$

Strain tensor

$$E^{(\alpha)} = \frac{1}{2} e_{ij}^{(\alpha)} \sigma_{ij}^{(\alpha)}$$

$$e_{ij}^{(\alpha)} = \frac{1}{2}(\partial_j u_{\alpha,i} + \partial_i u_{\alpha,j})$$

$$\sigma_{ij}^{(\alpha)} = \frac{E}{1+\nu}[e_{ij}^{(\alpha)} + \frac{\nu}{1-2\nu} e_{ll}^{(\alpha)} \delta_{ij}]$$

α =(Si soit Ge)

Boundary conditions :Stress and strain are continuous at the Si/Ge interface, no dislocations.

$$\boldsymbol{u}_s = \tilde{\boldsymbol{u}}_f \text{ and } \boldsymbol{\sigma}_s \cdot \hat{\boldsymbol{z}} = \boldsymbol{\sigma}_f \cdot \hat{\boldsymbol{z}} \quad \text{at} \quad z = 0$$

$$\boldsymbol{\sigma}_f \cdot \hat{\boldsymbol{n}} = 0 \quad \text{at} \quad z = h(x,y,t)$$

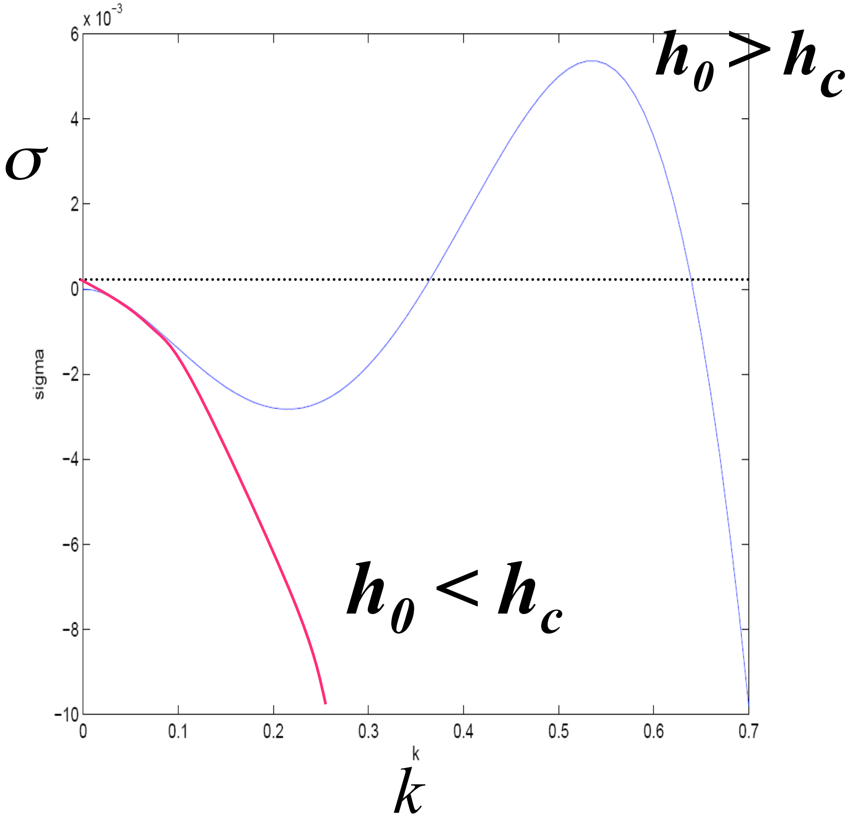
No stress at the free boundary
(non-linear geometrical conditions)

Linear analysis :

$$h(x,y,t) = h_0 + \delta h\, e^{i\mathbf{k}.\mathbf{r}+\sigma t}$$

$$k = |\mathbf{k}|$$

$$\sigma = -c_w k^2 + (\frac{\delta a}{a})^2 k^3 - k^4$$



$$\gamma(h) = \gamma\,[1 + c_w \exp(-h/\delta)]$$

Flat film stable
for $h_0 < h_c$

Small slope equation

$$\frac{\partial h}{\partial t}=\frac{\partial^2}{\partial x^2}\left\{-\left[1+c_w f\left(\frac{h}{\delta}\right)\right]h_{xx}+\frac{c_w}{\delta}\frac{f'(h/\delta)}{\sqrt{1+h_x^2}}-\omega_1\mathcal{H}(h_x)\right.$$

$$\left.+\,\omega_2(2hh_{xx}+h_x^2)+\omega_2^*(2\mathcal{H}\{[h\mathcal{H}(h_x)]_x\}+[\mathcal{H}(h_x)]^2)\right\},$$

Singular term

Nonlinear nonlocal terms which prevents the singularity.

$$\gamma(h)=\gamma_f[1+c_w f(h/\delta)]$$

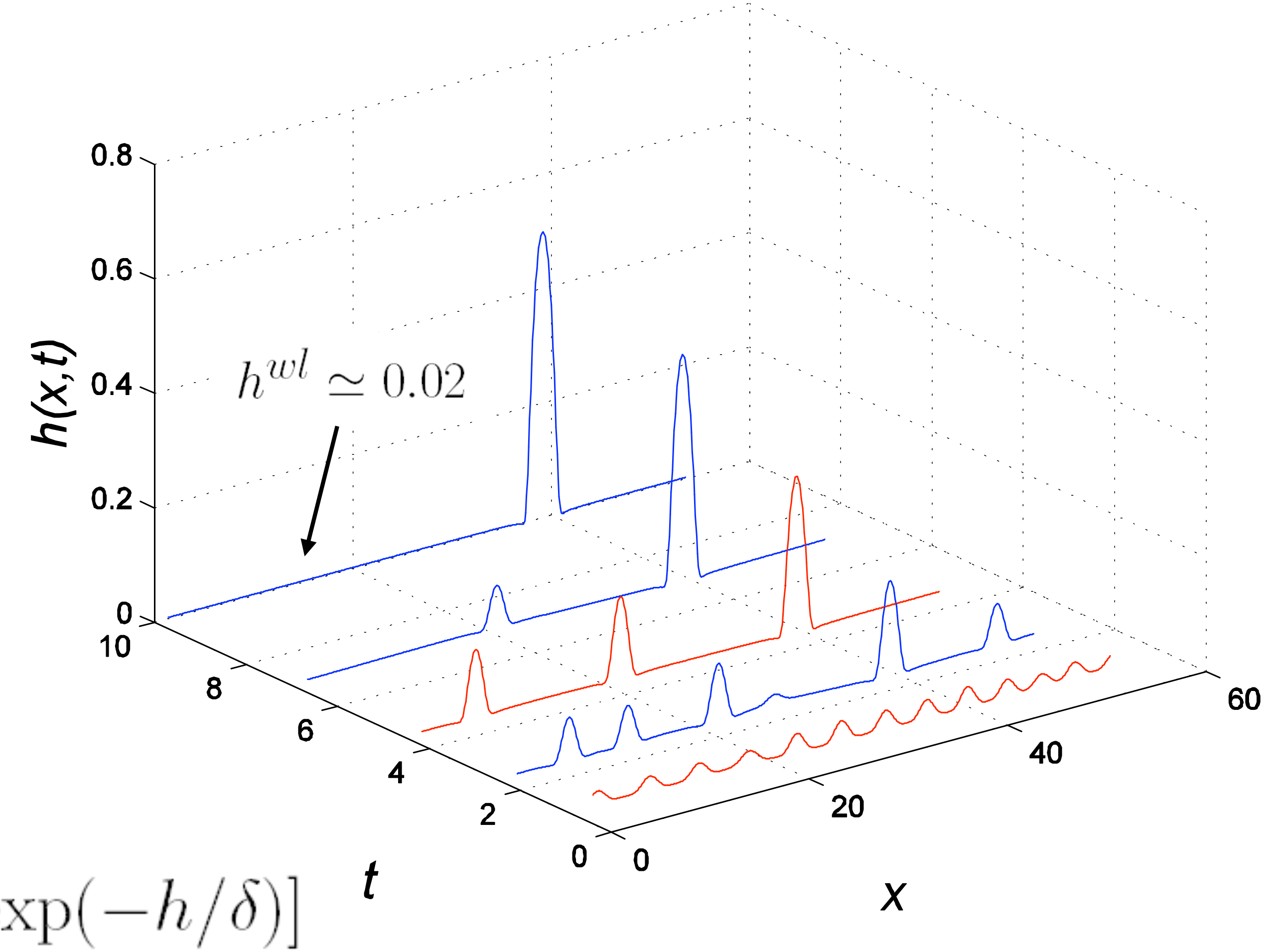
$$f(\xi)=\exp(-\xi)$$

f is the wetting potential

$$\mathcal{H}[h_x]=\mathcal{F}^{-1}\{|k|\mathcal{F}[h]\}$$

H is the Hilbert transform, multiplication by k in Fourrier Space

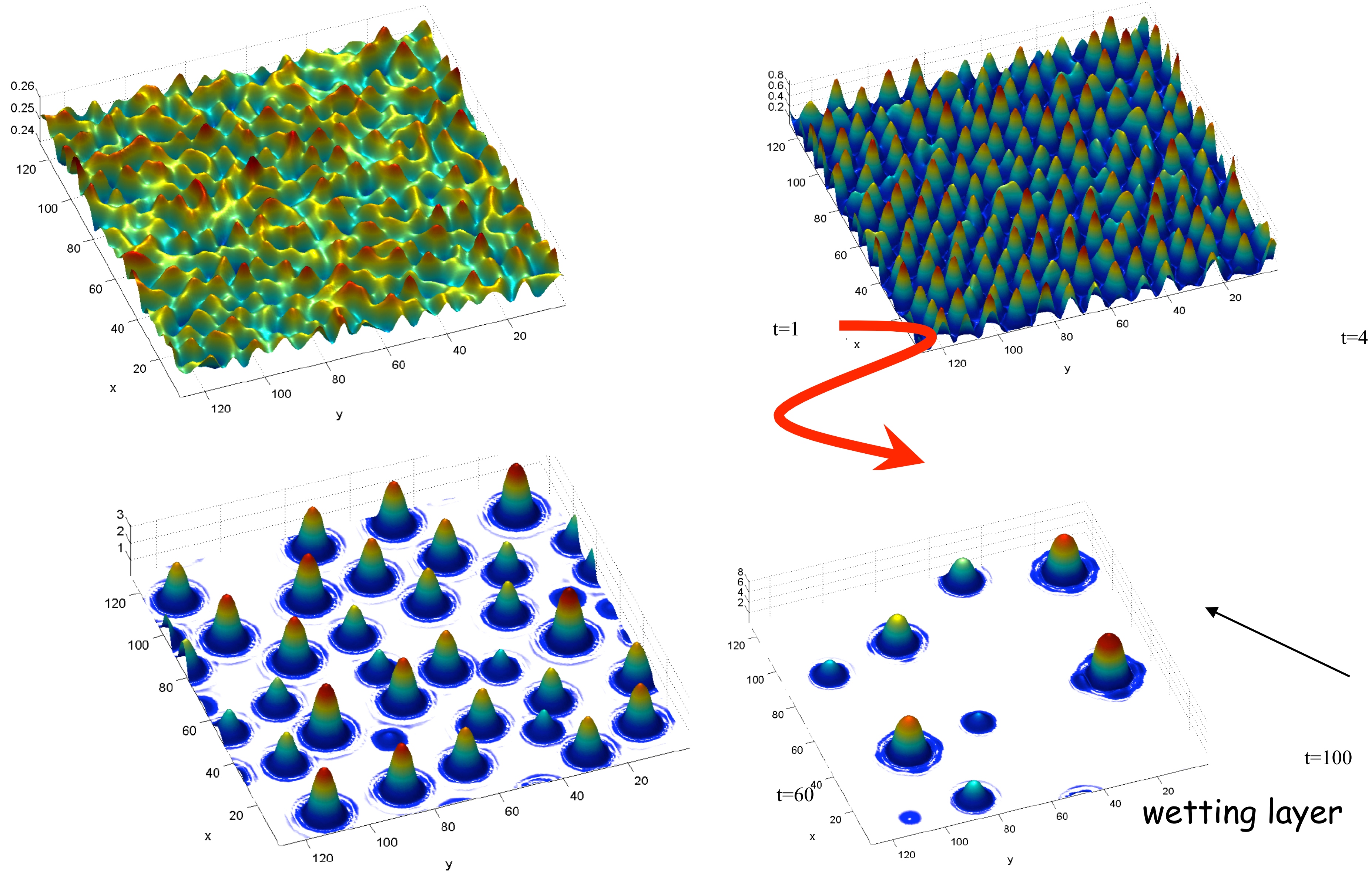
NO singularity when BOTH wetting (small, not diverging) & non-linear non-local effects are considered



$$\gamma(h) = \gamma\,[1 + c_w \exp(-h/\delta)]$$

$$c_w = 0.1$$

Numerical Simulations using Spectral Methods

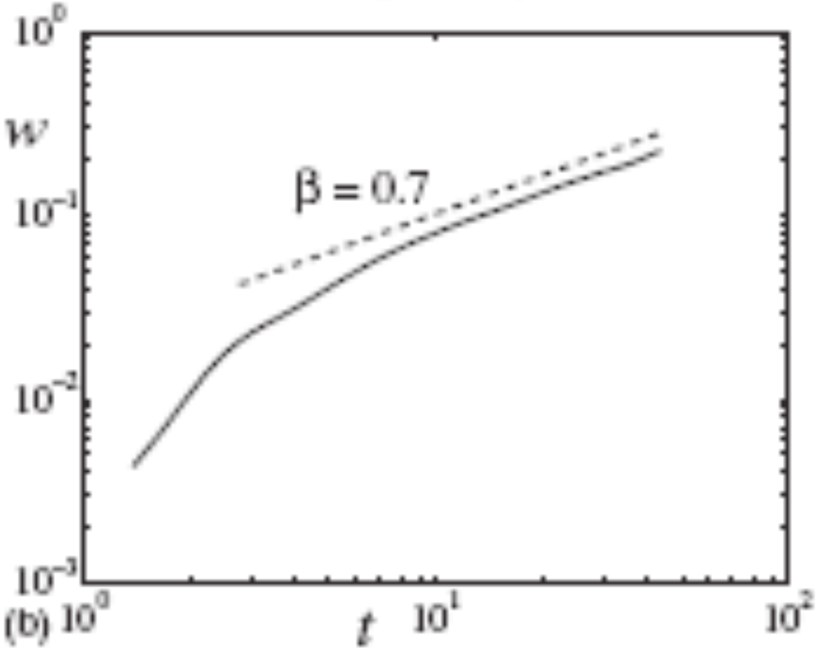


wetting layer

Non-interrupted coarsening

Large islands grow at
the expense of the small ones

Coarsening dynamics: numerical simulations



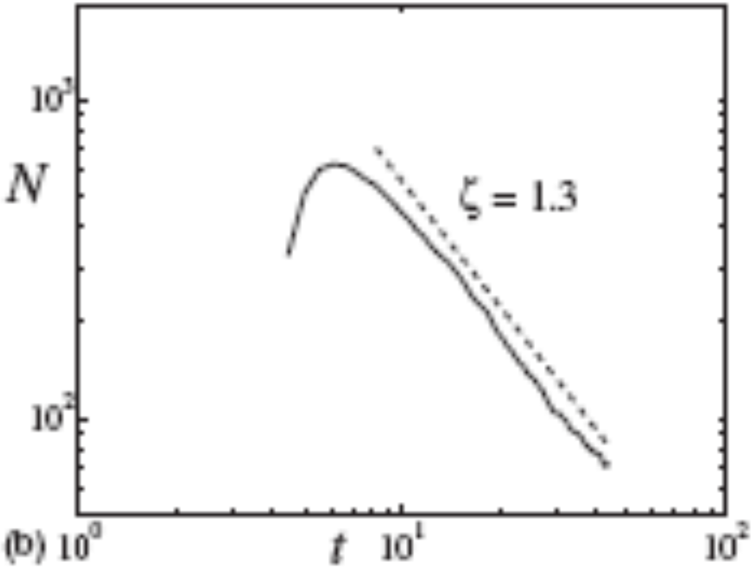
3D

1. roughness

$$w(t) = [\langle h^2 \rangle - \langle h \rangle^2]^{1/2}$$

$$w(t) \sim t^{\beta}$$

JNA, Frisch, Verga, PRB 07



2. Number of islands

$$N(t) \sim 1/t^{\zeta}$$

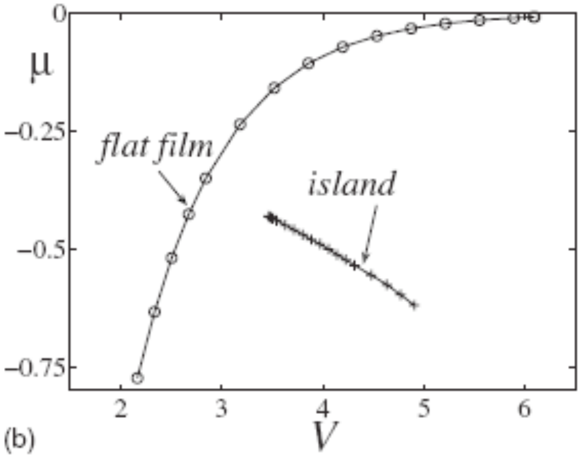
Dynamics of the coarsening

Some discussion about the coarsening exponent:

$$w(t) \sim t^{\beta}$$

$$N(t) \sim 1/t^{\zeta}$$

	Levine, Golovin, Davis, Voorhees PRB 07	Pang, Huang PRB 06	Aqua, Frisch, Verga PRB PRB 07
β	2.88	0 saturation	0.7
ζ	2.9	N/A	1.3



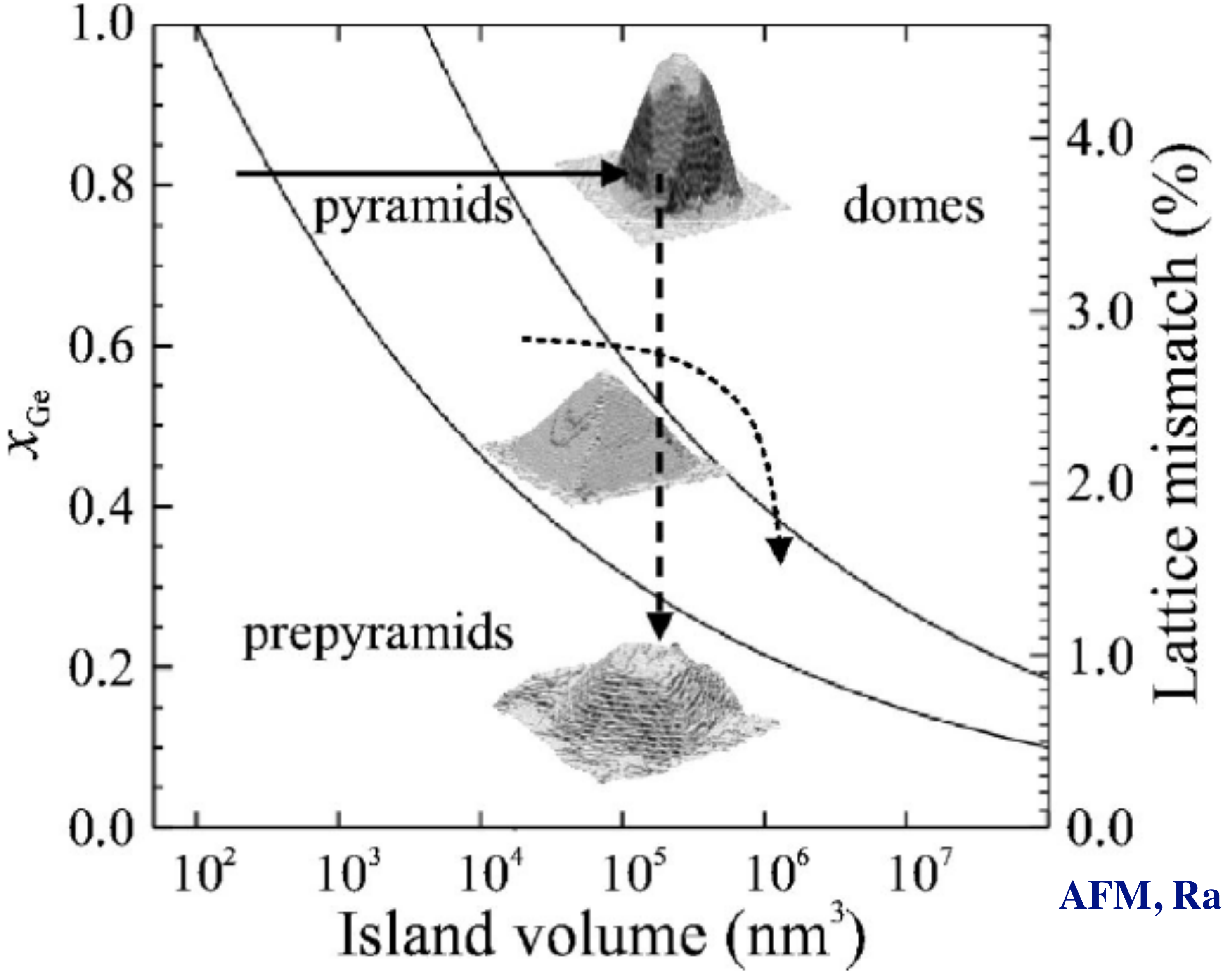
Annealing

Hypothesis :

No facetting :

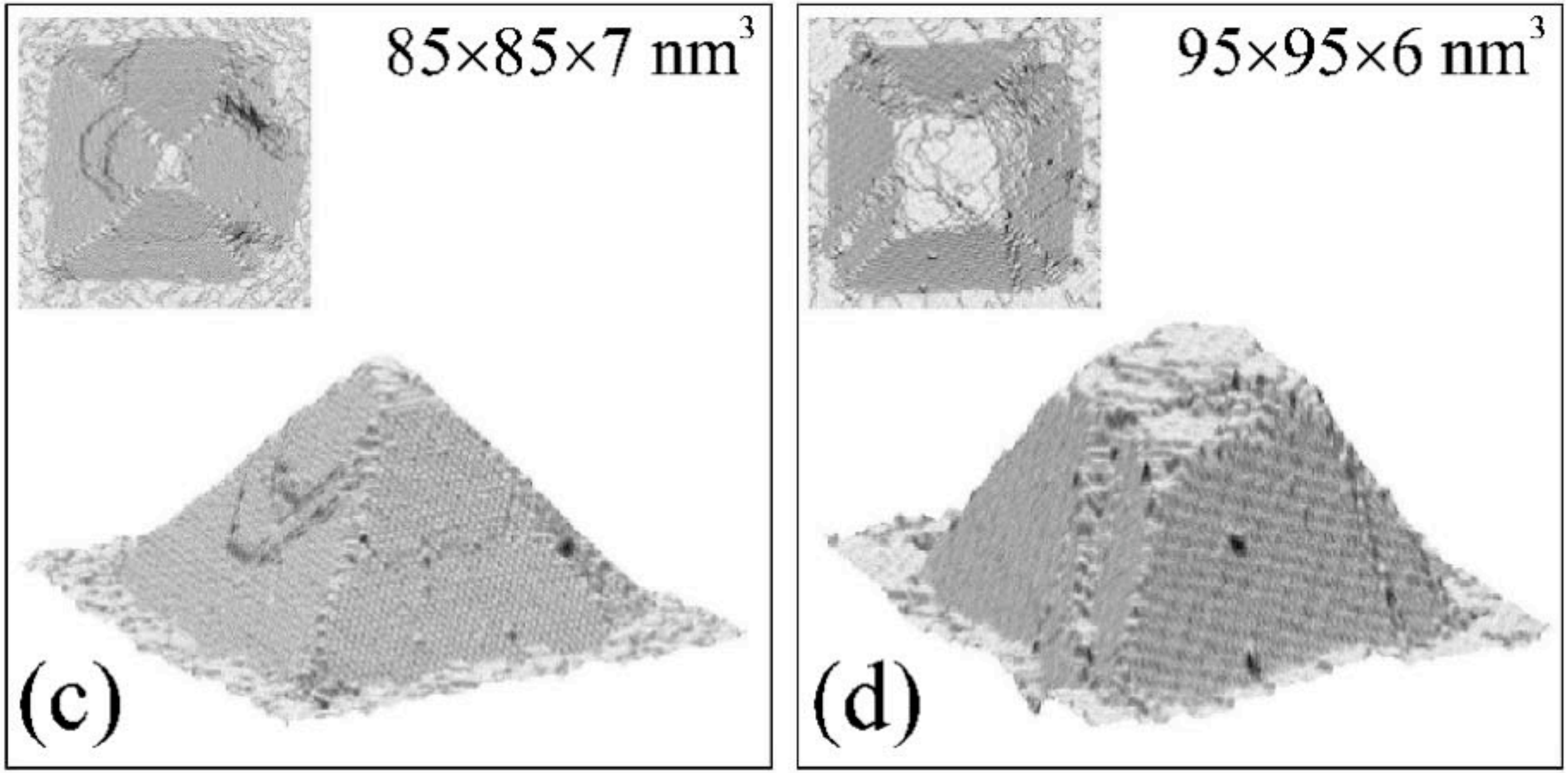
No alloying :

Silicon/germanium island are faceted



AFM, Rastelli, PRL

Silicon Germanium island



AFM, RMP 04, Rastelli,
the (105) is apparent

Surface energy anisotropy

$$\mathcal{F}^{s} = \int \gamma(h, \boldsymbol{n}) \sqrt{1 + |\boldsymbol{\nabla} h|^{2}}\, d\boldsymbol{r}$$

$$\mathcal{F}^{el} = \int_{z<h(\boldsymbol{r})} \mathcal{E}^{el}(\boldsymbol{r}, z)\, d\boldsymbol{r}\, dz\,.$$

***n* is normal to the surface**

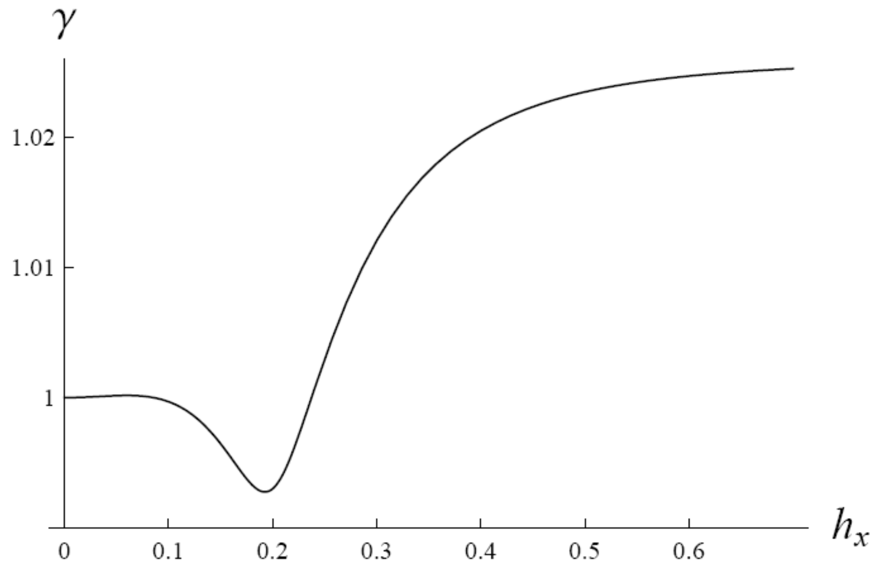
$F = F^{s} + F^{el}$

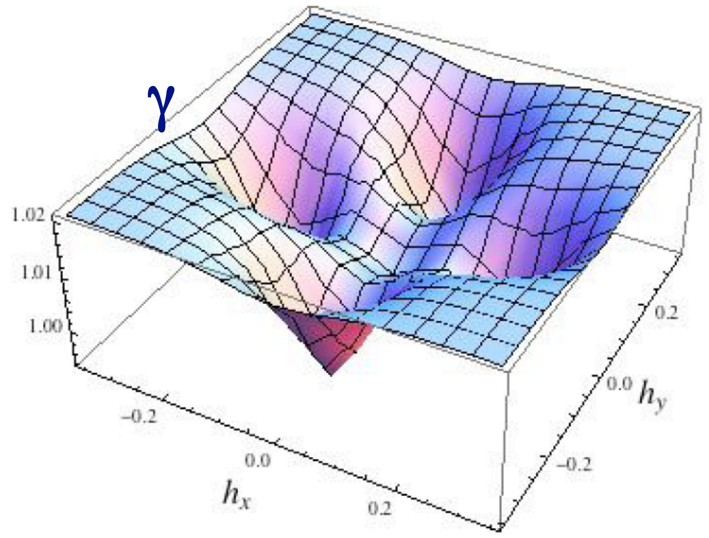
$$\mu = \delta \mathcal{F} / \delta h$$

The surface energy depends on the orientation and also on the elastic-strain.

We neglect the second effect but we take a minium for the (105) orientation.

Effect of the anisotropy of surface energy (Gamma Plot)



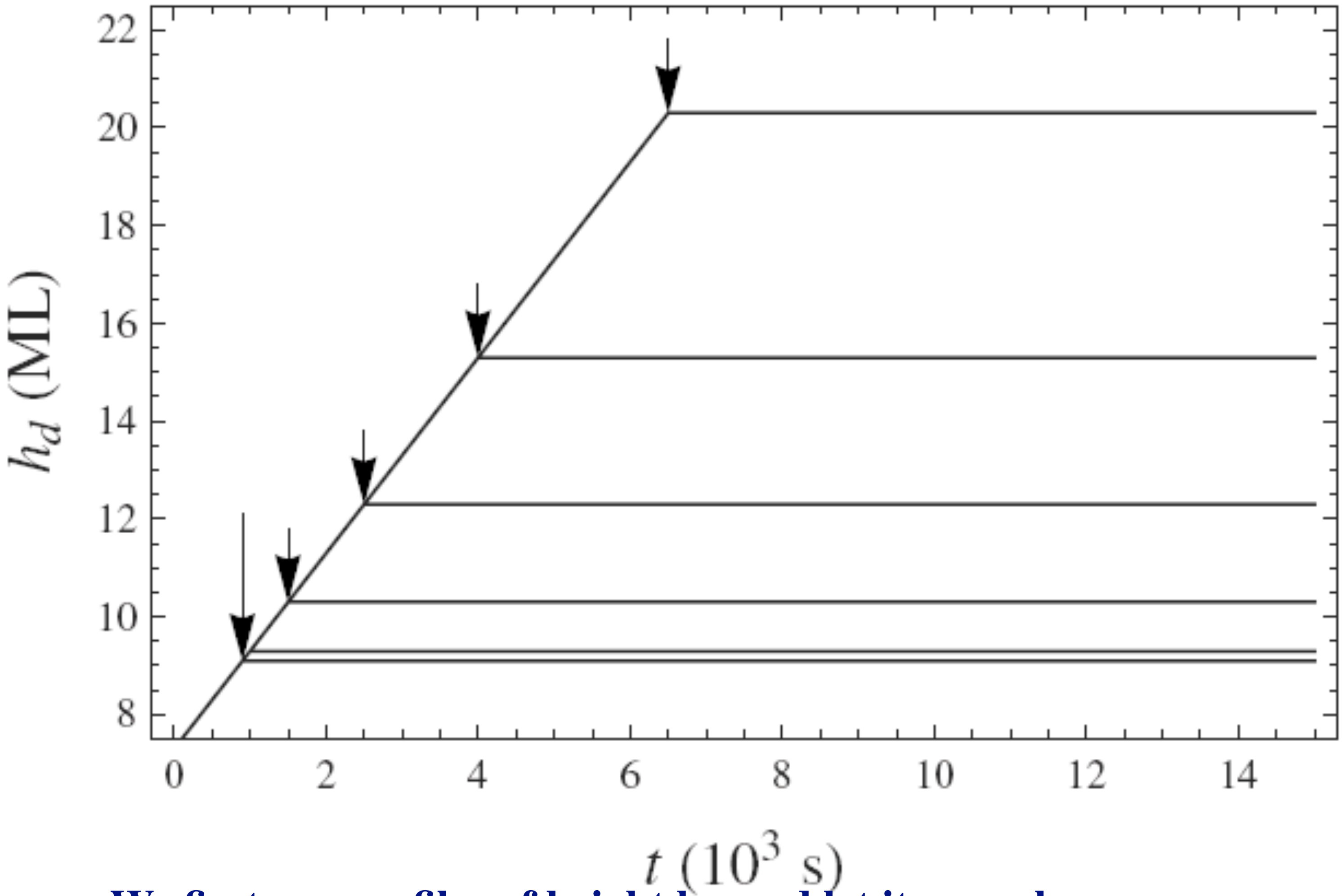


$$\gamma(h,\boldsymbol{n}) = \gamma_f[1 + \gamma_{\boldsymbol{n}}(\boldsymbol{n}) + \gamma_h(h)]$$

In a crystalline solid, the surface energy depends on the orientation $\gamma(n)$ and also on the elastic-strain.

Y. W. Zhang, Phys Rev B, 61, 2000

Numerical Protocol



We first grow a film of height h_d and let it anneal.

The deposited height h_d is the relevant parameter.

Evolution of the island density

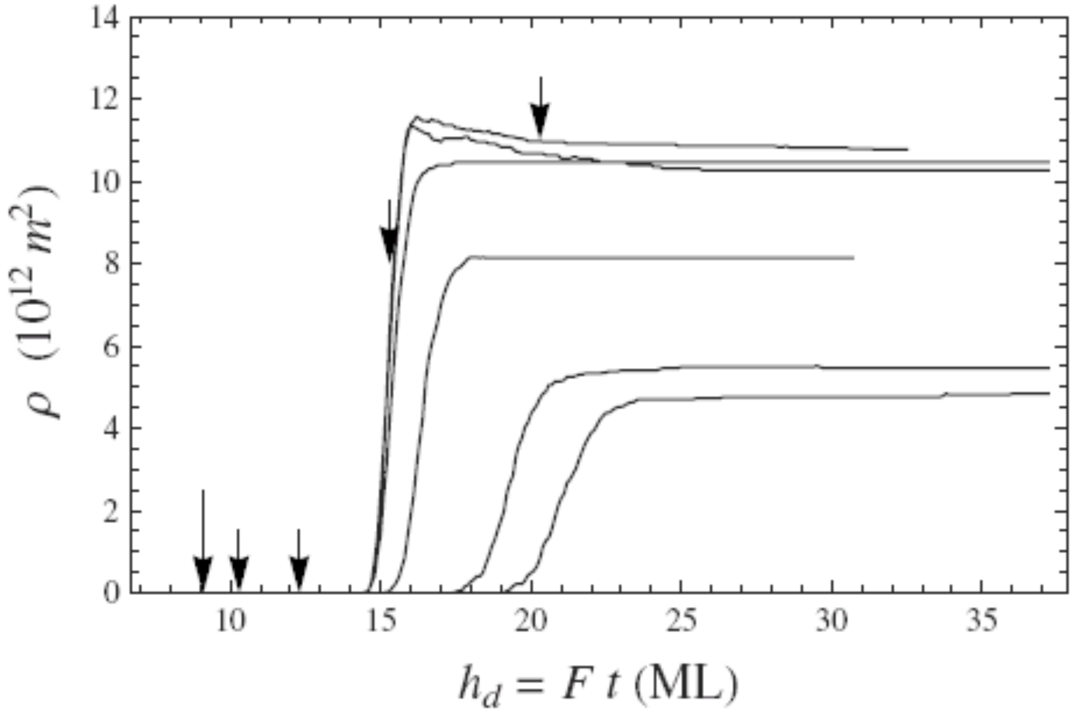
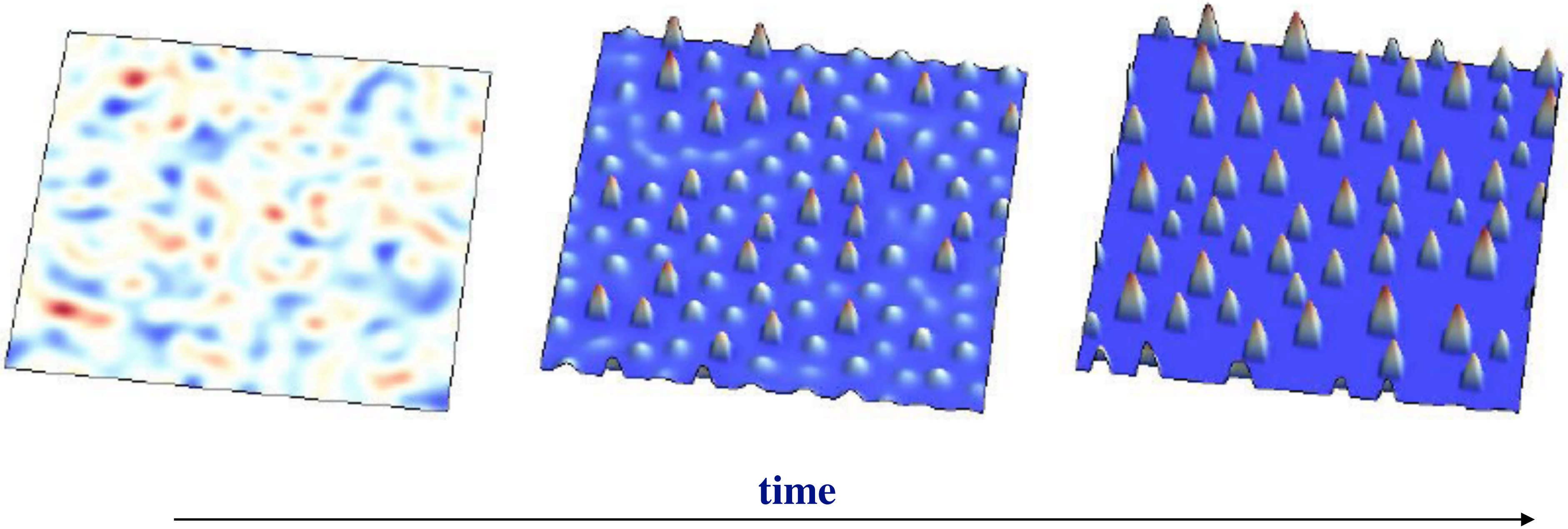


FIG. 8. Numerical results of Eq. (32). Evolution of the island density versus time for, from bottom to top, the cases (a, b, c, d, e, f).

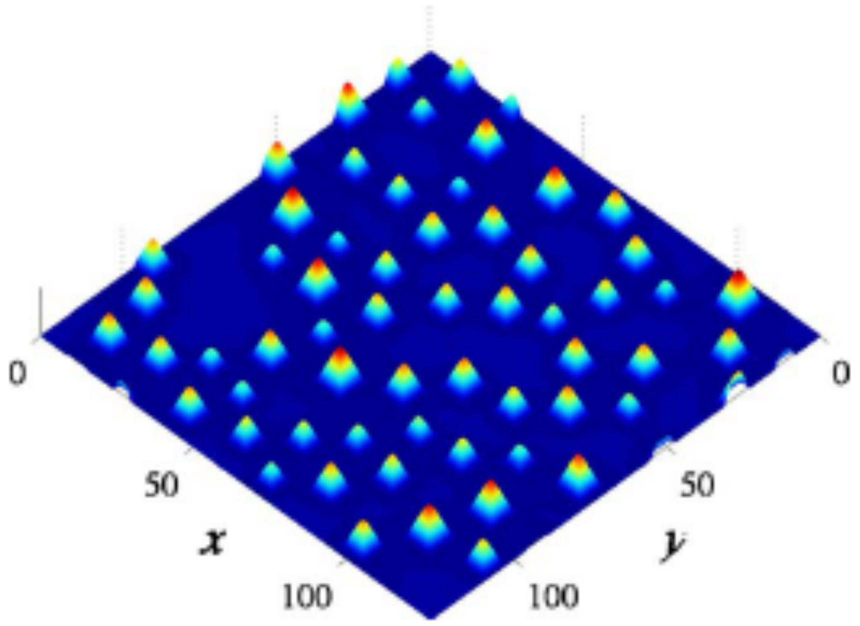
Time evolution



Top= 9 ML

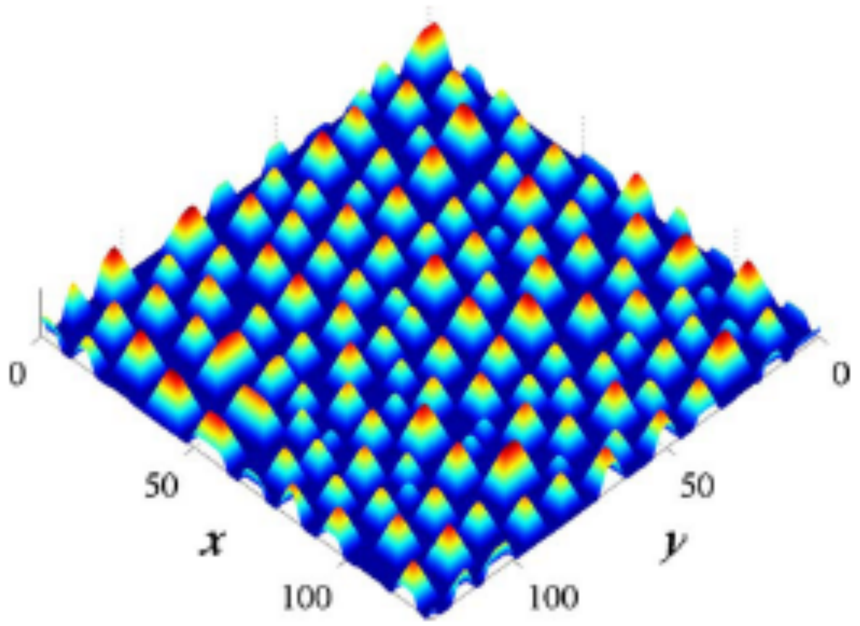
L=128 l_0

l_0=27 nm



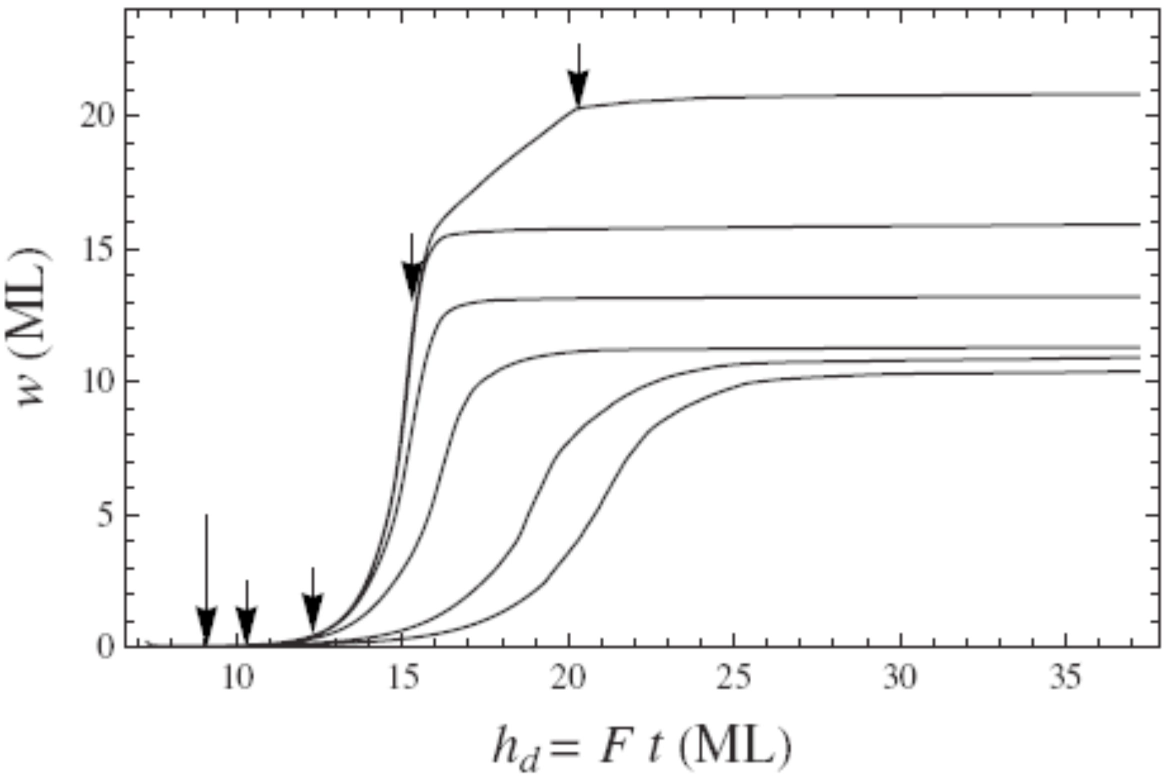
Bottom = 20.2 ML

Anneal time is 300 Minutes



Simulations

Evolution of the roughness

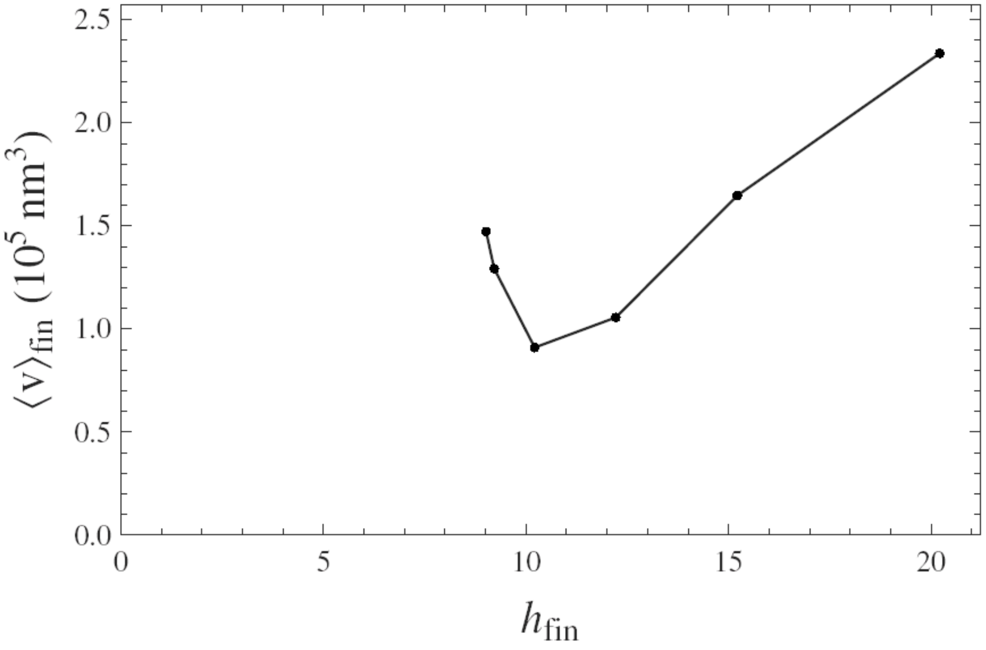


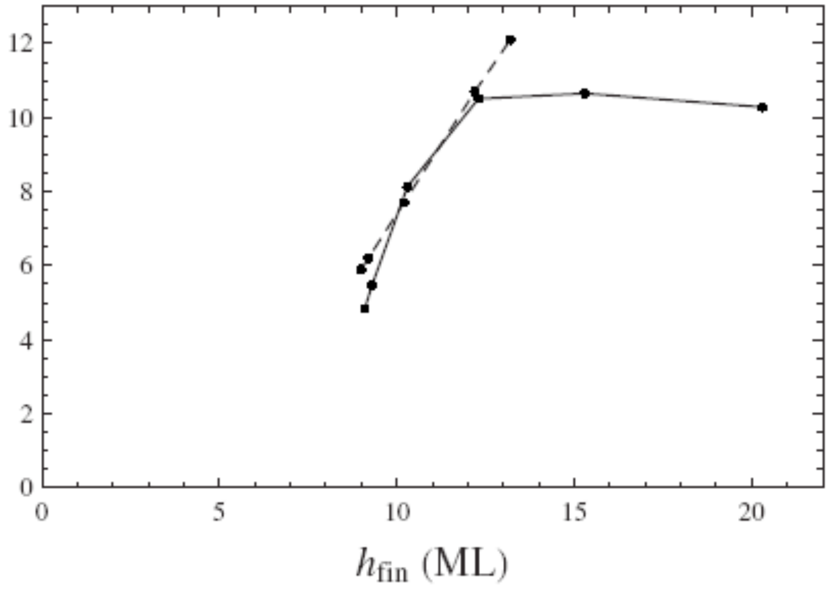
Coarsening is interrupted

Dots density and size can be controled: coarsening is interupted

Island Volume

density

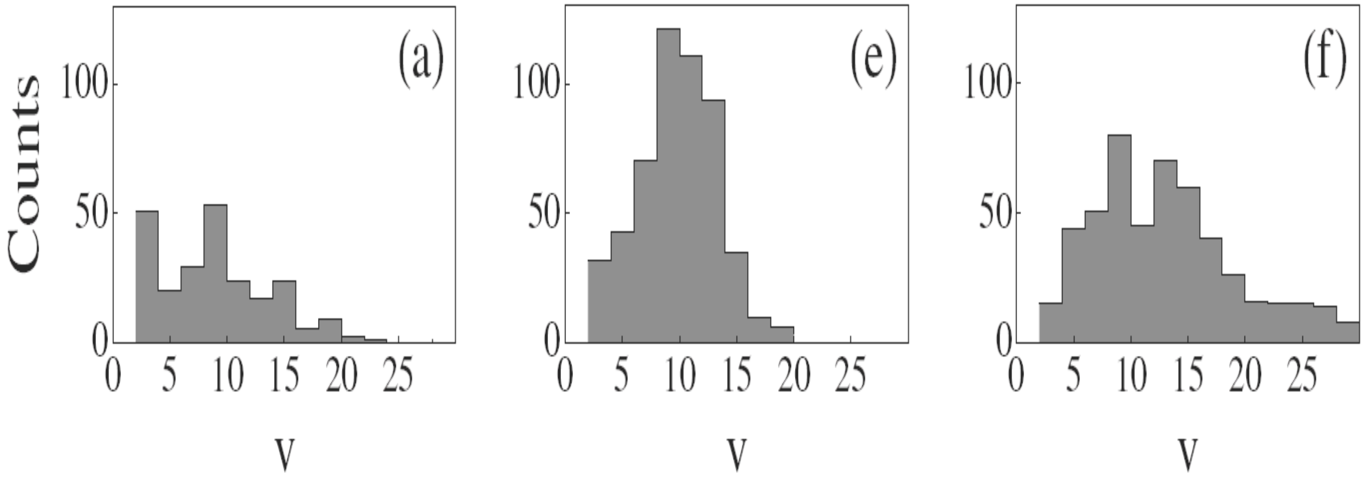




Numerical simulation

We can vary the dots density as a function of the deposited height

Distribution of island sizes



9ML **15 ML** **20 ML**

Dispersion of island size distribution: r.m.s.

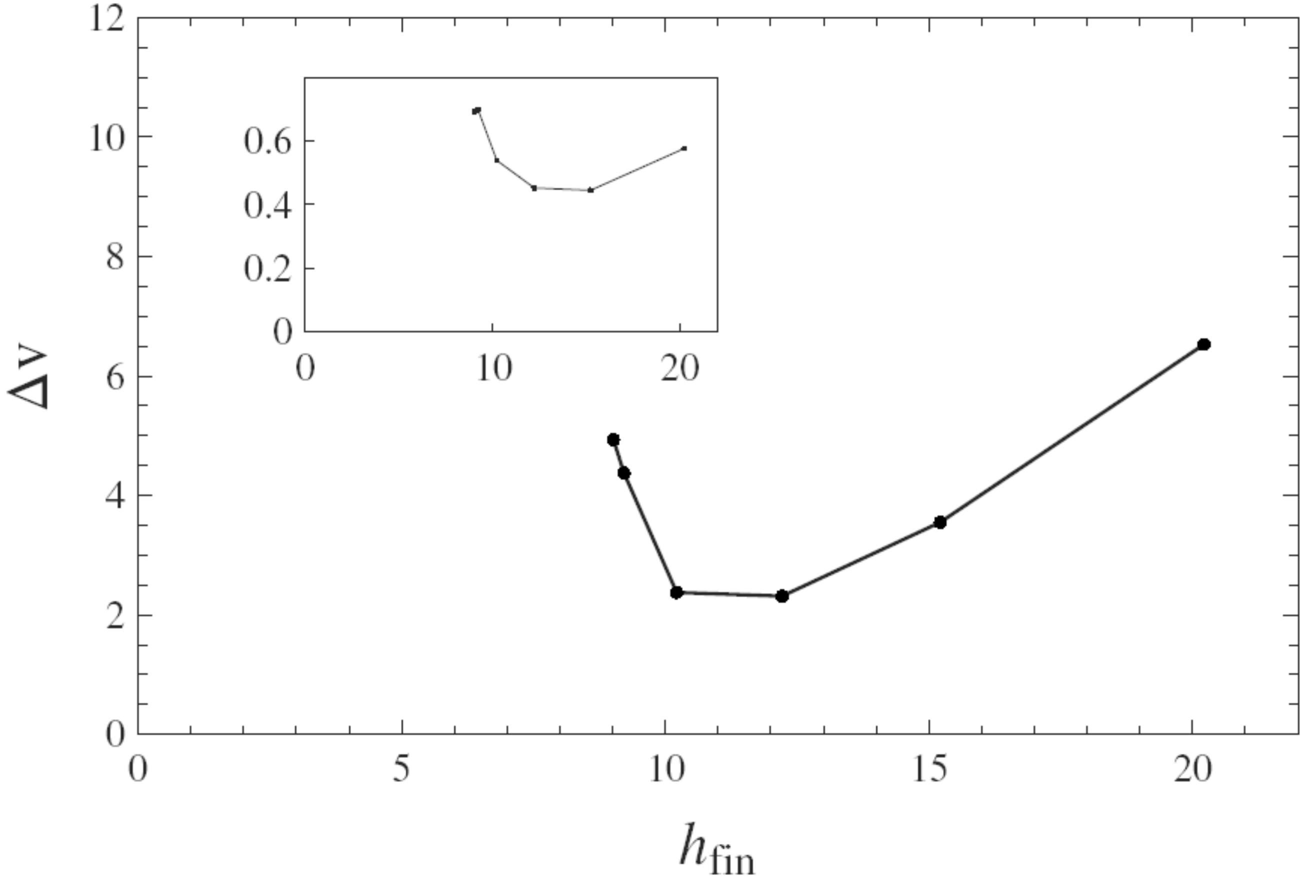
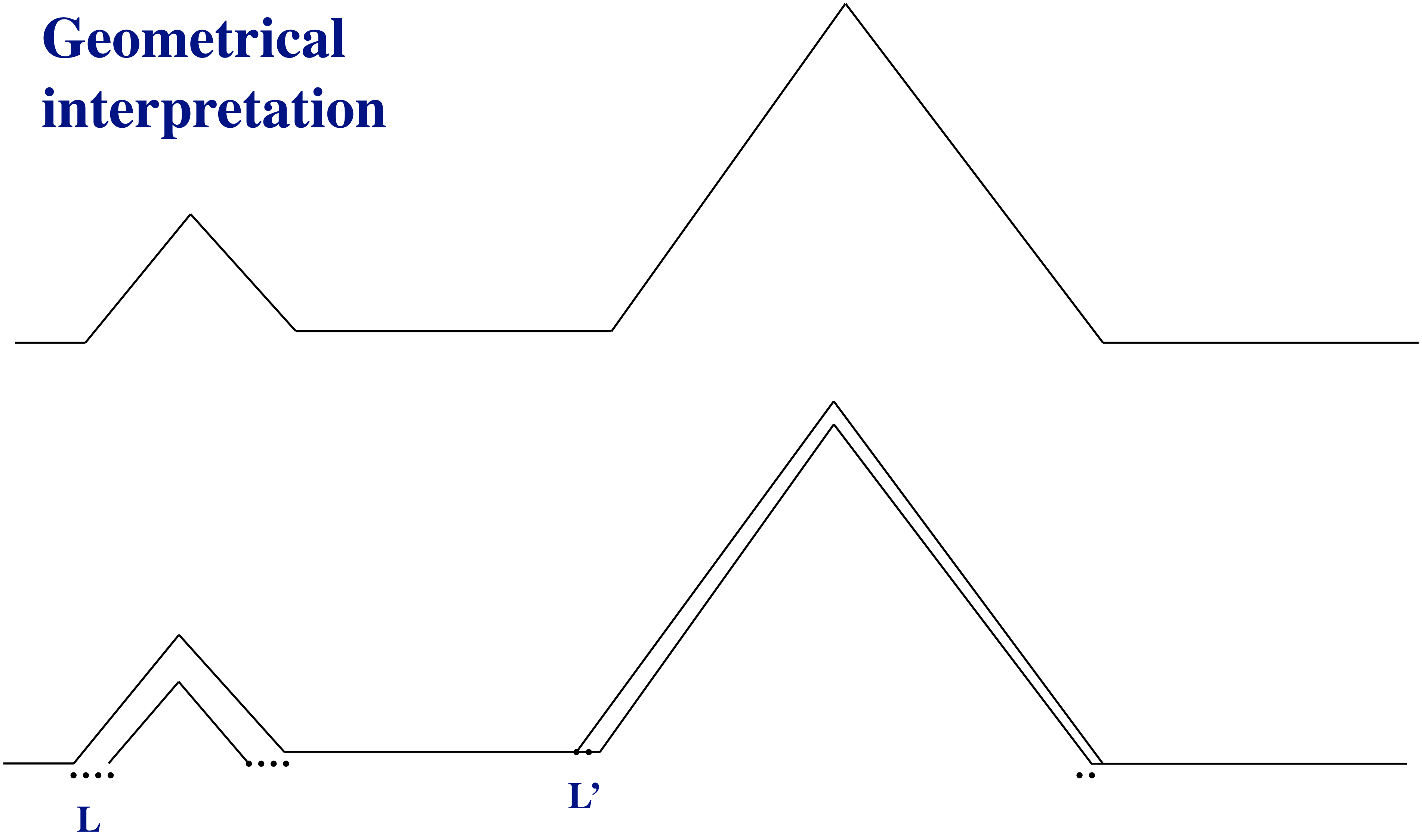


FIG. 14. Standard deviation Δv of the island size distribution as function of the amount of matter and (inset) relative width $\Delta v/\langle v\rangle$.

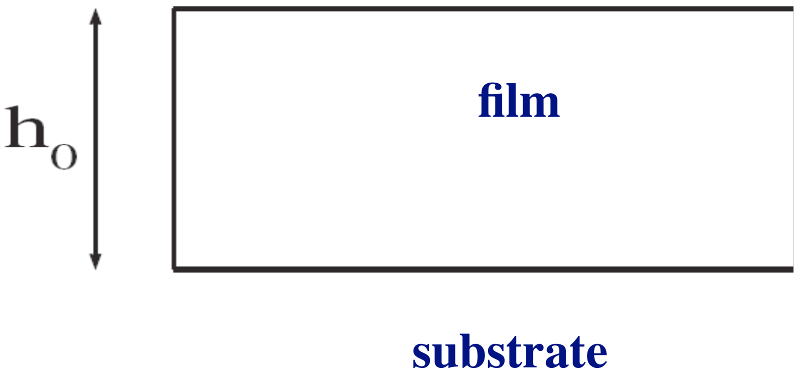
Geometrical interpretation

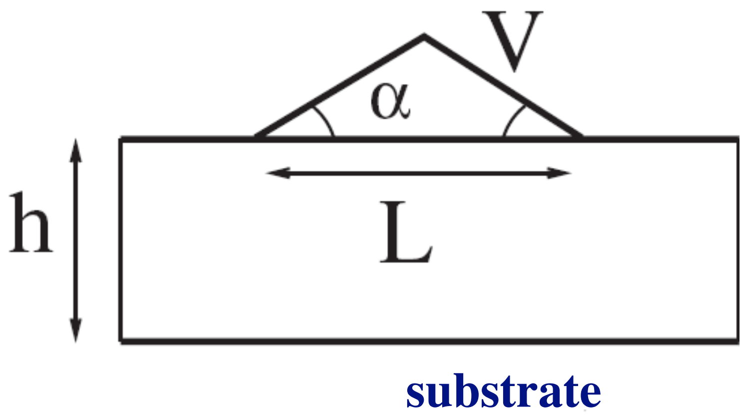


Aqua-Frisch,
2010, Phys Rev B
76

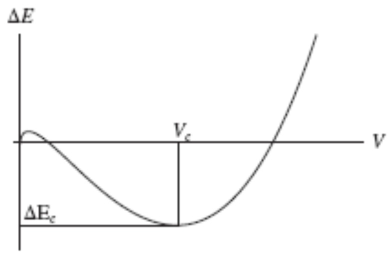
L > L’, the wetting energy increases, but the surface energy decrease and the elastic energy remains constant.

Energetic model





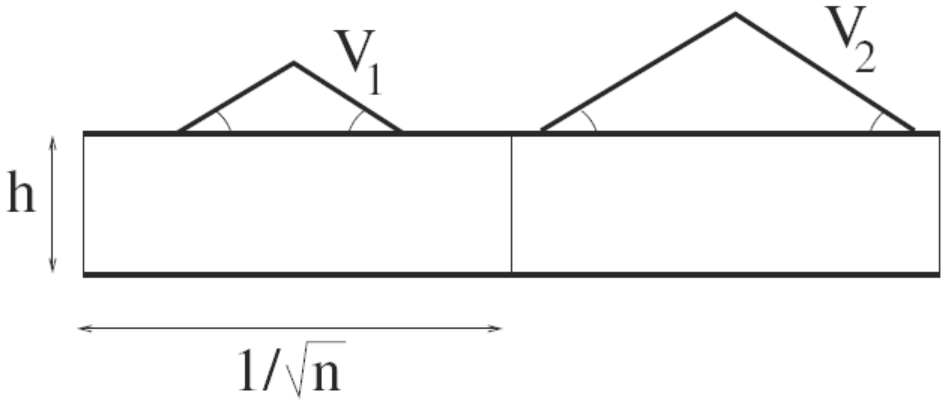
$$h = h_0 - nV.$$



$$\Delta E = \gamma_f L^2/\cos\alpha - L^2\gamma(h_0) + (1/n - L^2)[\gamma(h) - \gamma(h_0)] - \lambda_e V.$$

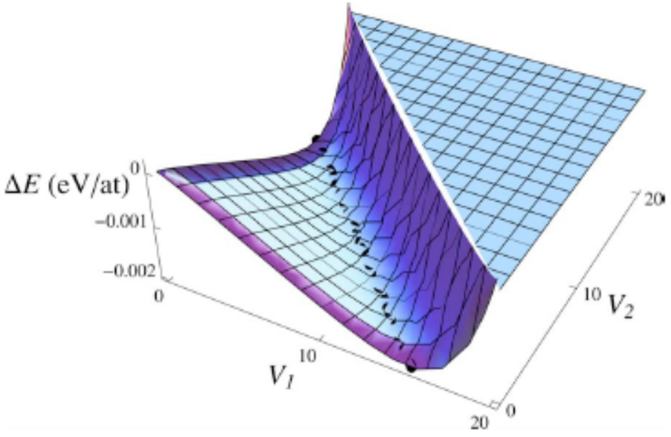
[43] L. G. Wang, P. Kratzer, M. Scheffler, and N. Moll, Phys. Rev. Lett. 82, 4042 (1999).

Two-island model



Two free parameters are: the height of the wetting layer,

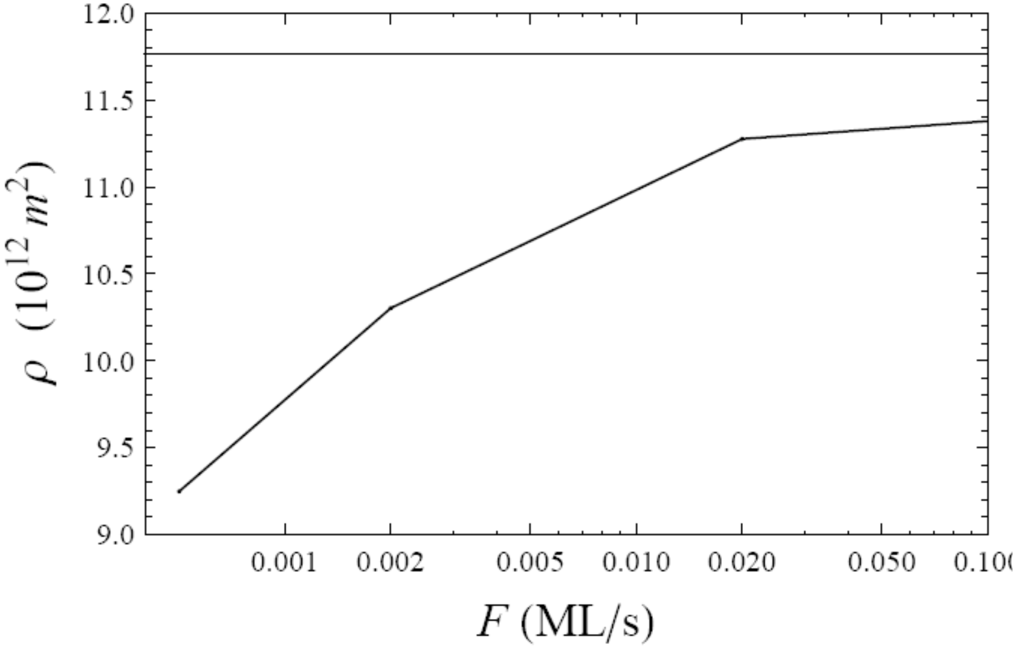
and the surface density of pyramids

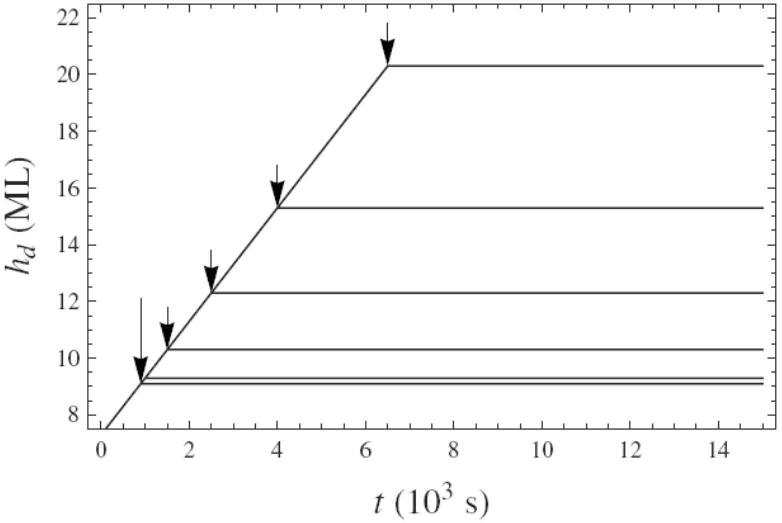


V1 = V2 is a valley wih a very small slope.

J.-N. Aqua, T. Frisch , PRB, 82, 085322, 2010

Effect of the flux





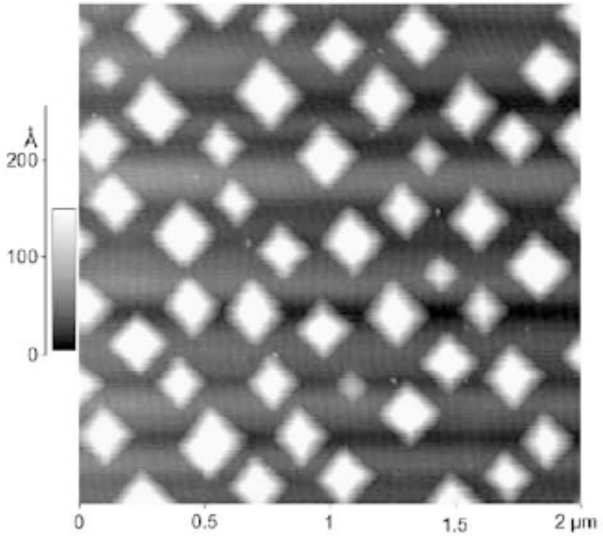
The flux does not really affect the density of island for $h_d = 11.7$

Experimental results

- $Si_{0.7}Ge_{0.3}$ annealed at 550 celcius for 54 hours for different deposited height.

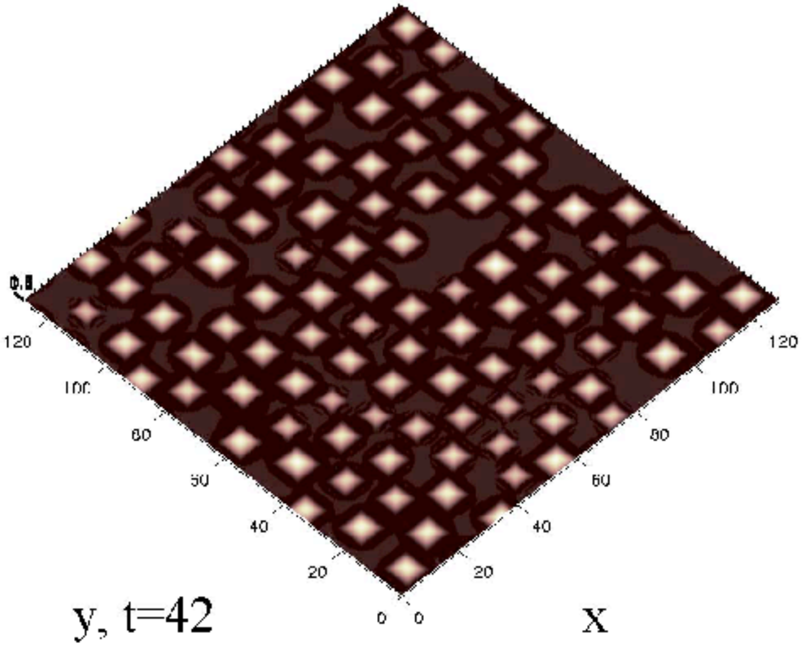
MBE group of Isabelle Berbezier

Interupted corsening is also observed experimentally



Experiments,I. Berbezier, 2002, J. Phys Cond Matters, SiGe/Si

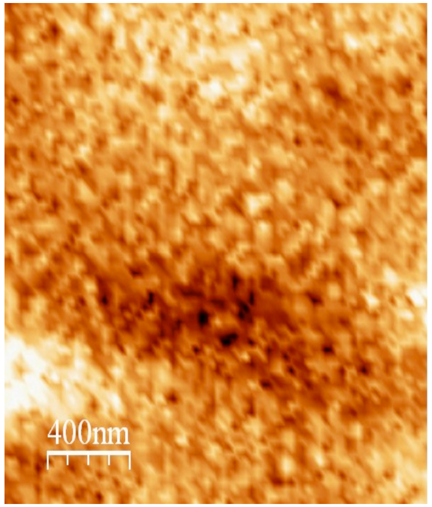
AFM



Numerical simulations

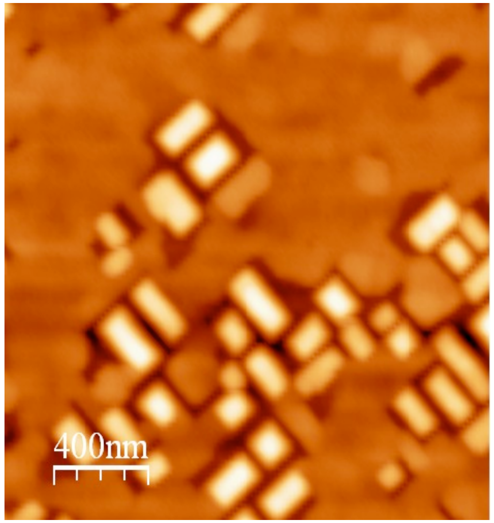
Experiments

Si0.70Ge0.30 550°C

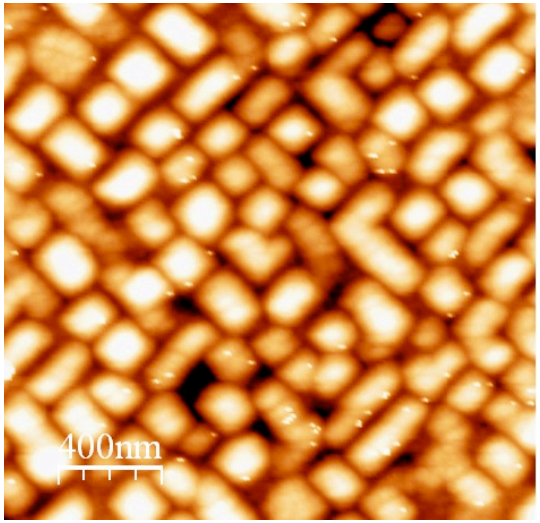


as grown

15.8 Monolayers



18 Hours annealing

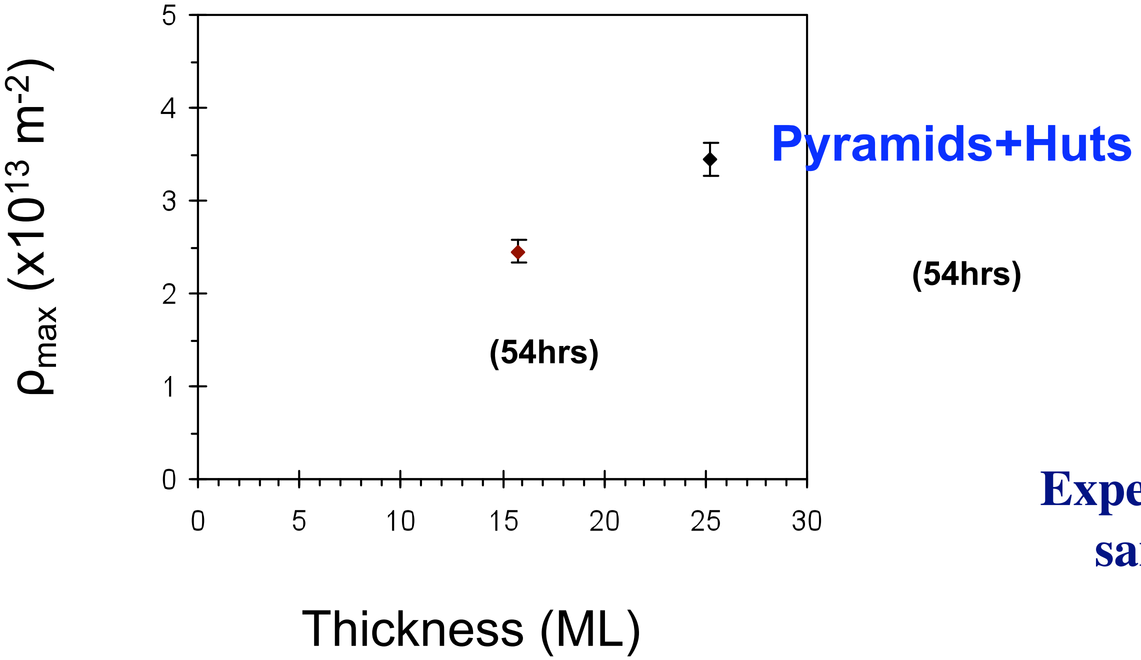


54 hours annealing

Time

→

$Si_{0.70}Ge_{0.30}$ (550°C)
ρ_{max} as function of the amount of matter



Experiments density falls with the same order of magnitude as the theory but a more detailed comparaison is needed:

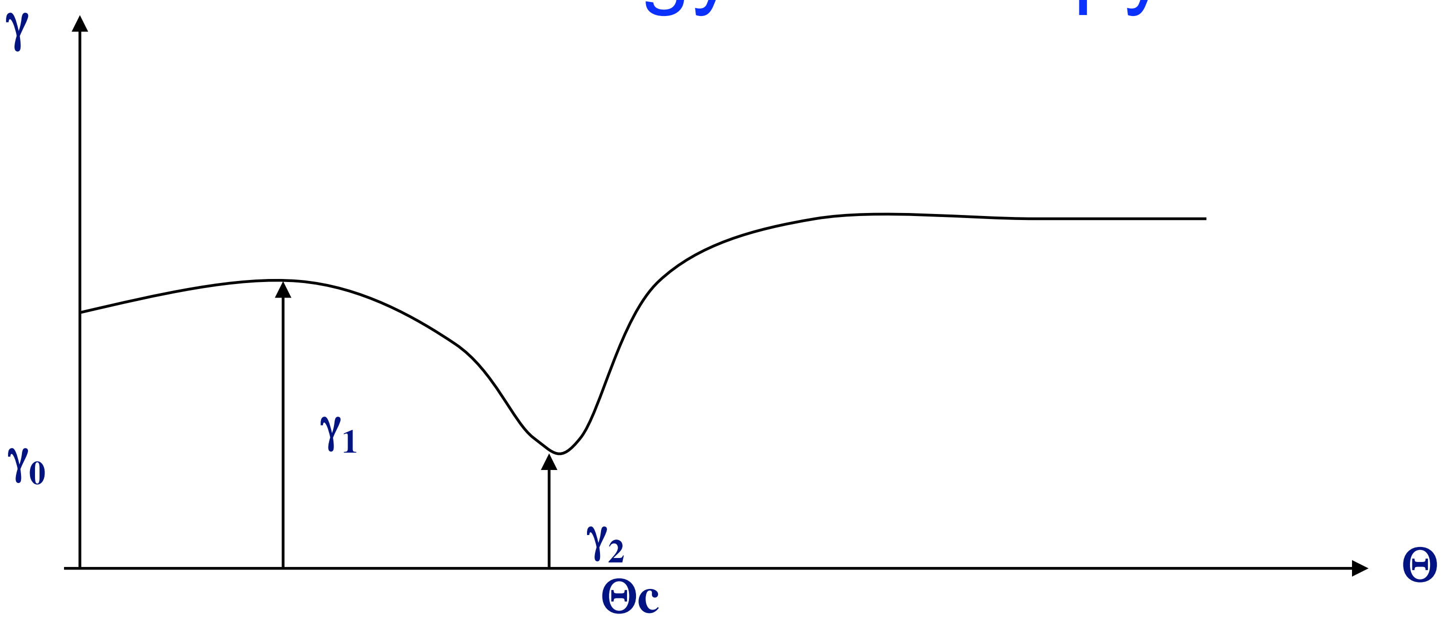
In particular, we are doing Ab_Initio calculation to extract the value of the diffusion coefficient (V. Oison)

1ML SiGe30% = 3.169A

Conclusion

- The elastic instability has a rich nonlinear regime
- We derived a fast methods for Stransky-Krastanov growth modeling in the instability regime
- Coarsening is interupted due to the interplay between anisotropy of surface energy and the wetting effect.
- We may control the dots size on Si/Ge by varying the deposited height and the strain

How sensitive is the dynamics on the effect of surface energy anisotropy ?



Question: For which values of γ_2/γ_0 the dynamics changes from non-interupted coarsening to interupted coarsening?

Is the sharpness at Θ_c is important

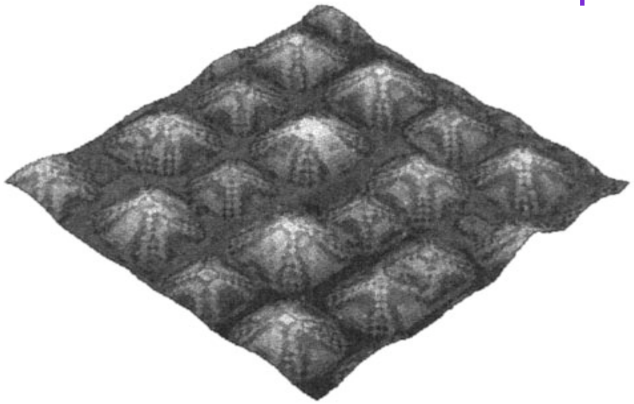
Close the instability threshold, it can be possible to compute a bifurcated solution and to verify the existence of periodic solutions (Landau expansion with anisotropy). One ingredient is period-doubling or tripling

Spencer, Voorhees and Tersoff, 2001,Tersoff, APL, 2003 Tu and Tersoff, PRL 2004,Tu and Tersoff, PRL 2007

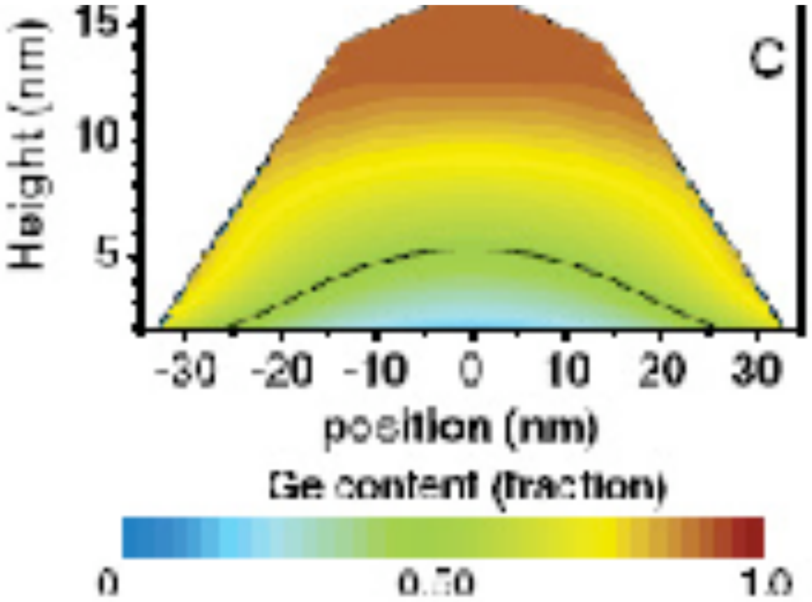
Perspectives on alloying.

- Alloying phenomena during Si/Ge growth, effect of surface segration effect,
- Application are on the III/V semiconductor.
- Nonlinear coupling between the compositional and the morphological instabilies. The alloys concentration is spatially inhomogenous and it has an impact on the opto-electronic propreties.
- Electron Phase microscopy analysis of alloys composition (P. Donnadieu, SIMAP, Grenoble, and I. Berbezier IM2NP)

What is the island composition ?



Floro **et al**, PRB 99



Medeiros-Ribeiro, PRL 2008, ESRF, Synchroton X

Collaborators: **Adrien Gouye, Isabelle Berbezier, Antoine Ronda, Alberto Verga.**

Relevant Publications :

J-N Aqua, T. Frisch and A. Verga, Phys Rev B, 2007
J.-N Aqua, T. Frisch, Phys Rev B, 2008, (Elastic Kinetic Monte-Carlo, island size distributions)
J.-N Aqua, T. Frisch and A. Verga, Phys Rev E 2010 (Flux effect)
J.-N Aqua, T. Frisch, Phys Rev B (2010)

Graduate Student: Xian Bin Xue, and Philippe Gaillard

Si-Ge growth of FIB patterned subsrtate

Compositional and morphological coupling