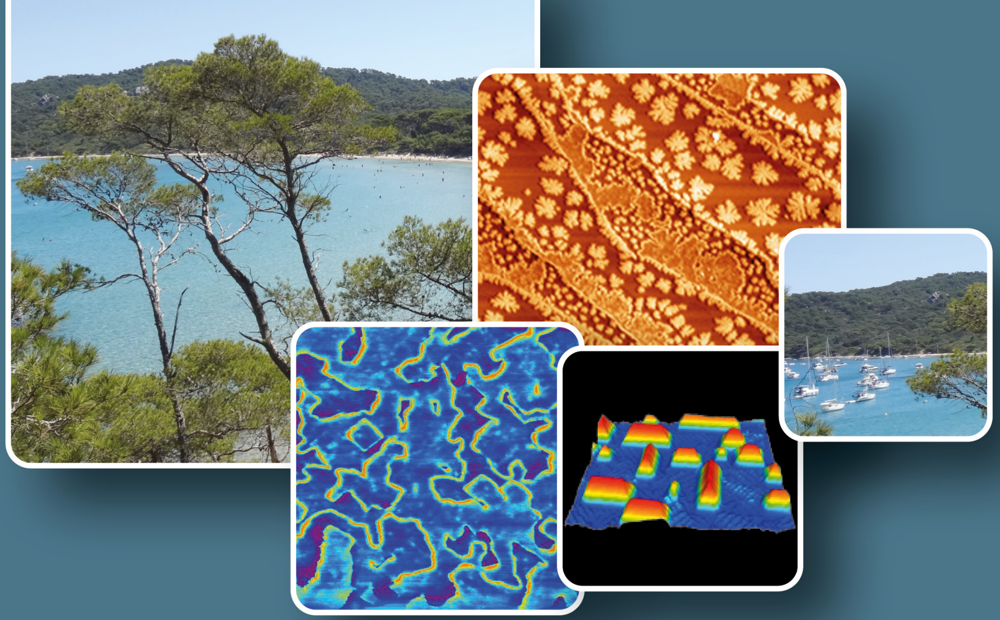


Summer school on Epitaxy

MATEPI 2025

Porquerolles June 22-27 2025

Organizing Committee

Mathieu Abel , Jean-Noël Aqua
Thierry Baron , Hélène Carrere
Ulrike Lüders, Laurence Méchin

Location

Hôtel Club IGESA - Rue de la Douane
Île de Porquerolles - 83400 HYÈRES

Speakers

Alberto Pimpinelli, Jean-Noël Aqua, Noëlle Gogneau, Alexandre Arnoult, Jean-Christophe Harmand, Matthieu Jamet, Guillaume Saint-Girons, Michele Amato, Delphine Lagarde, Anne Ponchet, Ulrike Lüders, Julien Brault, Eric Tournier, Hélène Carrere, Clément Mercking

Topics

Theoretical concepts
Experimental description
Characterization
Properties of nanostructure
Technological application

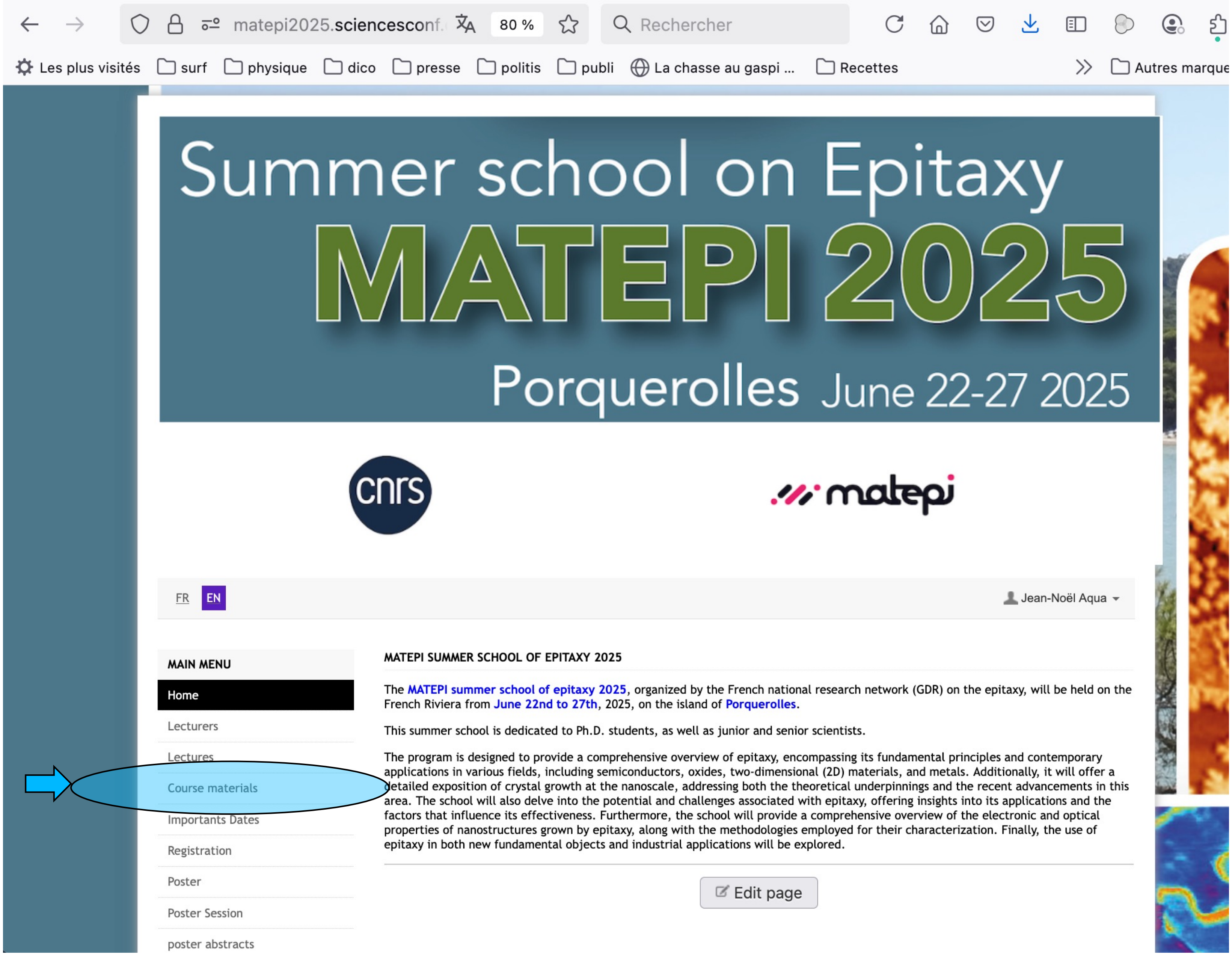
Registration at:

matepi2025.sciencesconf.org

Graphic conception: Cécile Duflot, INSP - © Frédéric Ducarme, INSP

	Monday 23rd	Tuesday 24th	Wednesday 25th	Thursday 26th	Friday 27th
8h30-10h	I.1 Crystal in and out of equilibrium Jean-Noël Aqua	III.1 Electronic and optical properties computation Michele Amato	I. 3 Growth on a stepped surface Alberto Pimpinelli	IV. 1 Electronic applications Julien Brault	IV. 2 Optical applications Fauzia Jabeen
10h-10h30 coffee break					
10h30-12h	II. 1 Instrumental epitaxy Noëlle Gogneau	III.3 Structural and chemical characterization in heteroepitaxy Philippe Venegues	IV.3 Oxides applications Clément Merckling	II. 7 Epitaxy of metals: concepts and comparisons Stéphane Andrieu	III.4 Novel properties of oxides Ulrike Luders
LUNCH					
14h-15h30	II. 2 In-situ monitoring Alexandre Arnoult	I.4 Growth modes Pierre Müller	OFF	II. 5 Epitaxial growth of 2D materials Matthieu Jamet	
15h30-16h coffee break					
16h-17h30	II. 6 Comparison of different epitaxy: oxides, semi-conductors, and oxides/semiconductors integration Guillaume Saint-Girons	Epitaxial growth of quantum nanostructures Frank Glas		III.2 Electronic, electric and optical properties: characterization Delphine Lagarde	
17h30-18h coffee break					
18h-19h30	I. 2 Nucleation and coarsening Alberto Pimpinelli	II. 3 Self-organization and surface structuration Noëlle Gogneau		round table : From fundamental reseach to industry Nicolas Vaissiere (3-5 Lab) Fabien Deprat (STMicro) Clément Merckling (IMEC)	
20h30-22h		POSTERS			

https://matepi2025.sciencesconf.org



MATEPI SUMMER SCHOOL OF EPITAXY 2025

The MATEPI summer school of epitaxy 2025, organized by the French national research network (GDR) on the epitaxy, will be held on the French Riviera from June 22nd to 27th, 2025, on the island of Porquerolles.

This summer school is dedicated to Ph.D. students, as well as junior and senior scientists.

The program is designed to provide a comprehensive overview of epitaxy, encompassing its fundamental principles and contemporary applications in various fields, including semiconductors, oxides, two-dimensional (2D) materials, and metals. Additionally, it will offer a detailed exposition of crystal growth at the nanoscale, addressing both the theoretical underpinnings and the recent advancements in this area. The school will also delve into the potential and challenges associated with epitaxy, offering insights into its applications and the factors that influence its effectiveness. Furthermore, the school will provide a comprehensive overview of the electronic and optical properties of nanostructures grown by epitaxy, along with the methodologies employed for their characterization. Finally, the use of epitaxy in both new fundamental objects and industrial applications will be explored.

Crystals in and out of equilibrium

Jean-Noël Aqua

I. Crystal growth vs equilibrium

II. Equilibrium
  1. Phase transition
  2. Phase separation
  3. Equilibrium shape of crystals
     a. Gibbs-Curie-Wulff theorem
     b. Wulff construction
     c. Kaischew construction
     d. Wulff today
     e. Continuous shape
     f. Continuous Wulff construction
     g. Inverse Wulff construction
  4. Atomistic crystal shapes
  5. Step fluctuations on vicinal surfaces
  6. Roughening transition
     a. Jackson model
     b. Morphologies
     c. Mean-field approach
     d. Correlations
     e. Renormalisation group
     f. Experiments

III. Out-of-equilibrium properties
  1. Ideal laws
  2. Kinetic Wulf theorem
  3. Kinetics-limited growth
     a. Nucleation
     b. Step growth
     c. Noise induced roughening
     d. Growth under constraint
  4. Theoretical tools for epitaxy

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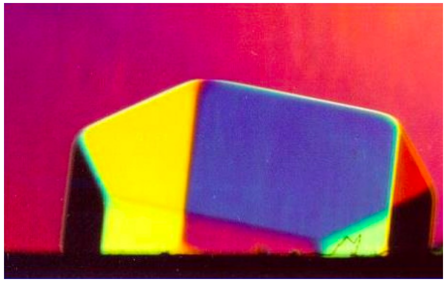
I. Crystal growth vs equilibrium

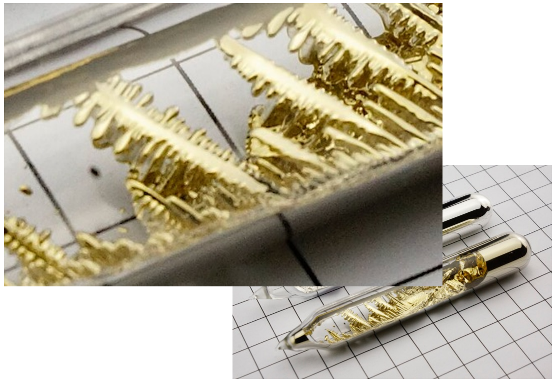
Crystalline forms result from **growth processes** and their proximity (or not) to equilibrium.

gypsum

H_2O

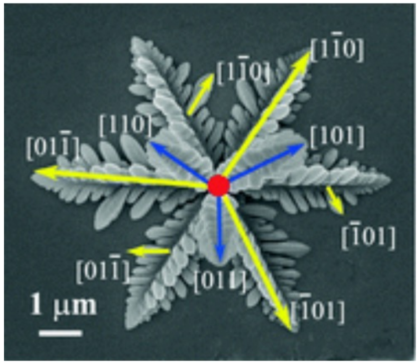


^4He



Cs

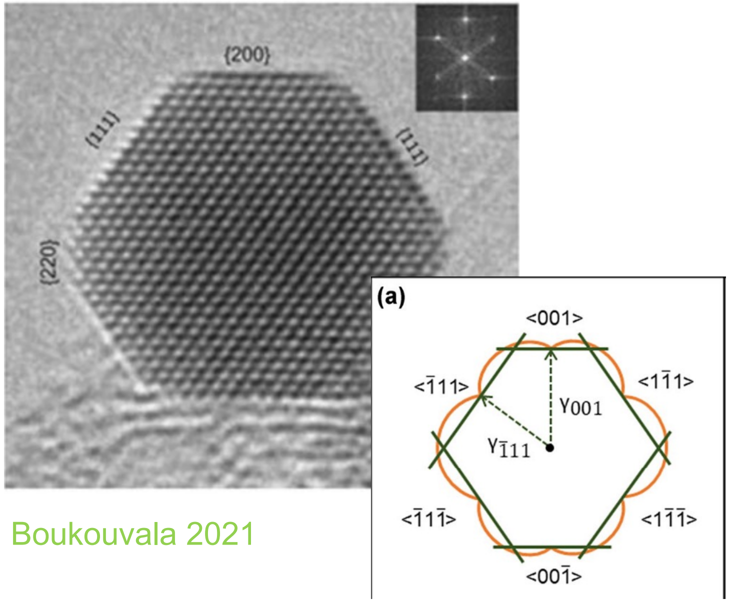
H_2O



Cu_2O

➡ NEED to understand **both** equilibrium and out-of-equilibrium physics

Crystalline forms are usually ***not*** at equilibrium but **metastable** (with a long lifetime) states



Boukouvala 2021

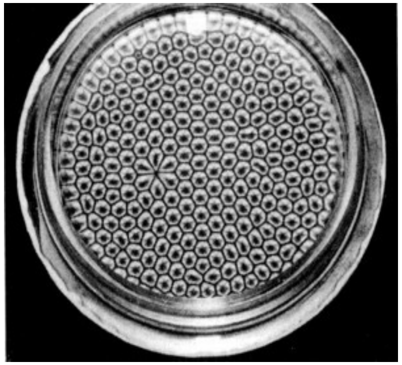
➡ NEED to understand **kinetic** processes

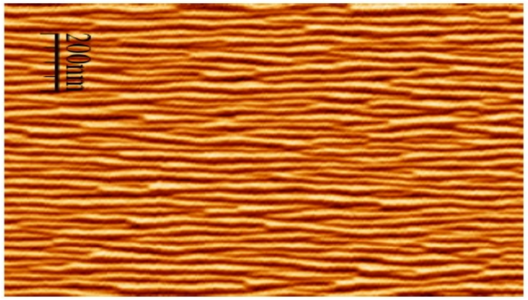
Self-organization (self-assembly) : *in out-of-equilibrium systems, a spontaneous order arises from local interactions between smaller parts of an initially disordered system.*
The process can be spontaneous when sufficient energy is available, not needing control by any external agent. It is often triggered by seemingly random fluctuations, amplified by positive feedback. cf Wikipedia

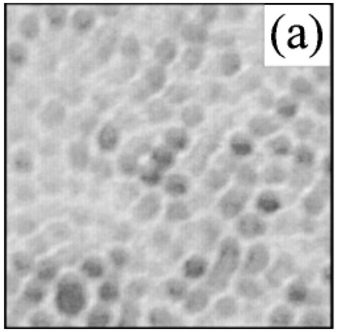
... Order arises from disorder in out-of-equilibrium

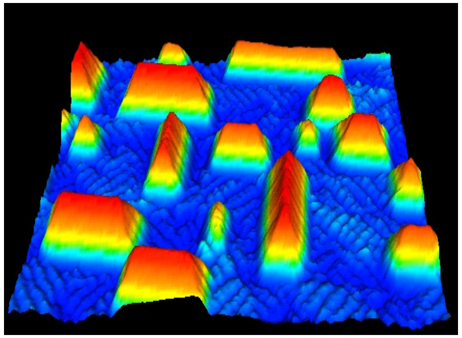
Related to theory of chaos and non-linear analysis

Ex : crystallization, thermal convection of fluids, chemical oscillation, animal swarming …









➡ NEED to understand **complex** systems

Crystals in and out of equilibrium

I. Crystal growth vs equilibrium

II. Equilibrium

1. **Phase transition**
2. Phase separation
3. Equilibrium shape of crystals
    a. Gibbs-Curie-Wulff theorem
    b. Wulff construction
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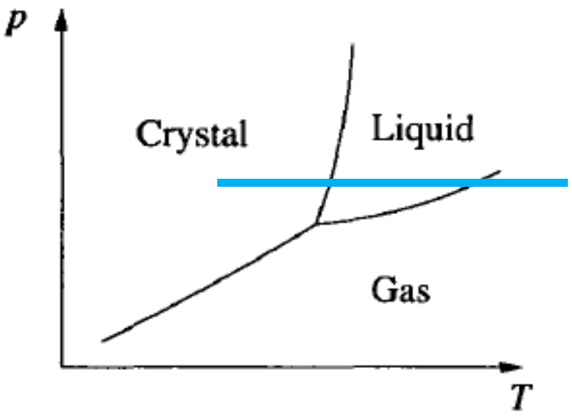
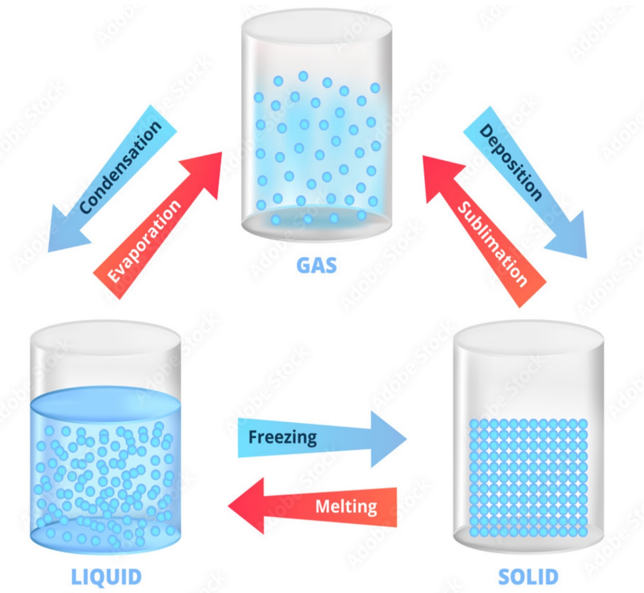
    d. Growth under constraint
4. Theoretical tools for epitaxy

II. Equilibrium

1. Phase transition

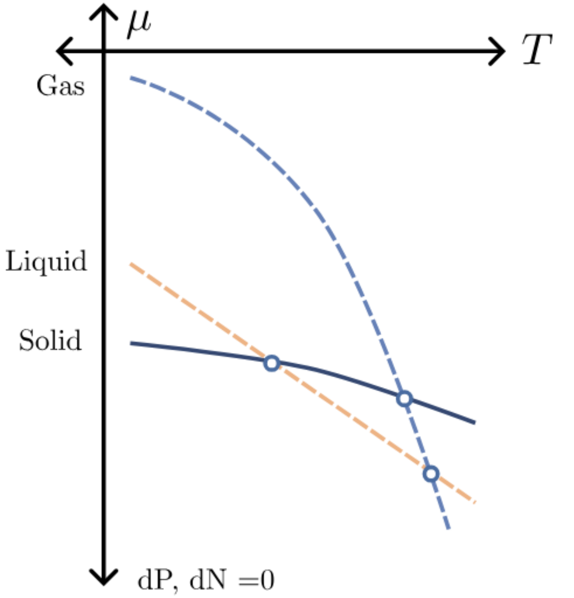
Phase transition
between solid/liquid/gas

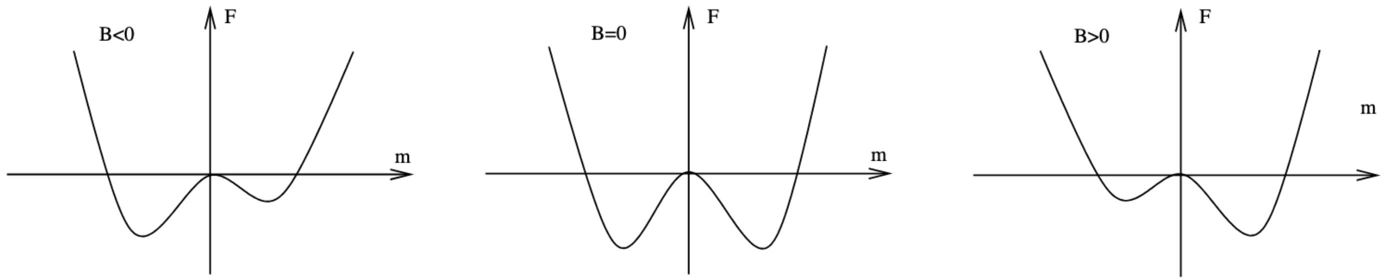




At equilibrium, at given P and T one has to minimize $G = U - T\,S + P\,V = \mu\,N$

- ✓ at low T, energy dominates : $\mu_S < \mu_L$
  the solid is the equilibrium state
- ✓ at high T, entropy dominates : the fluid wins

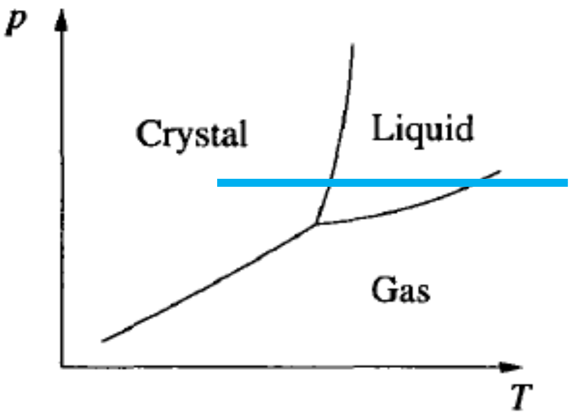


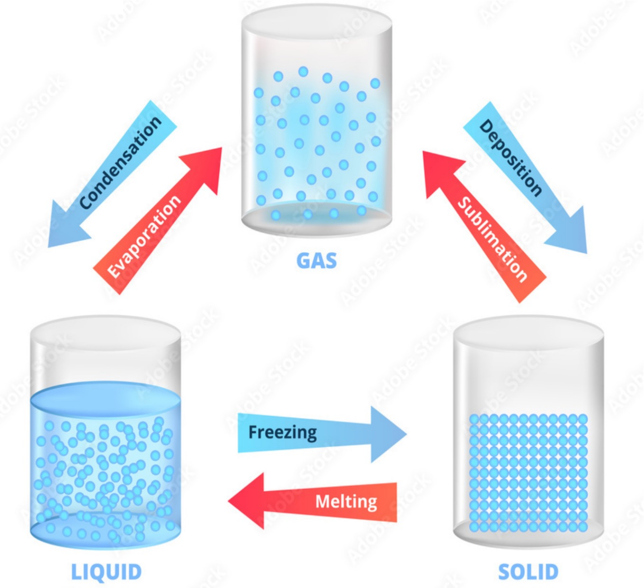


II. Equilibrium

1. Phase transition

Phase transition
between solid/liquid/gas





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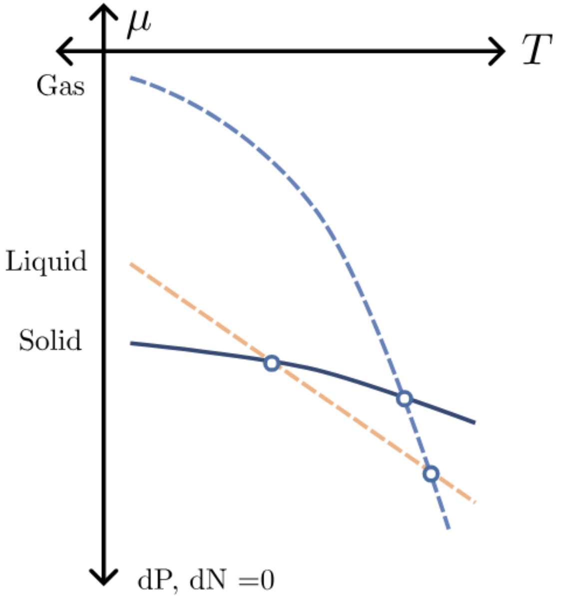


Phase separation occurs when $G_L(T_M, P) = G_S(T_M, P)$

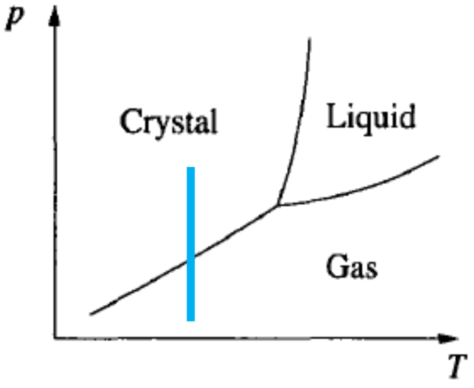
One defines the latent heat : $L = T_M \Delta S$

$$\left.\frac{\partial G_L}{\partial T}\right|_P - \left.\frac{\partial G_S}{\partial T}\right|_P = -\frac{L}{T_M}$$

➡ first order phase transition : discontinuity in the first derivative of the thermodynamic potential

II. Equilibrium properties

1. Phase transition



Phase transition
between solid/liquid/gas

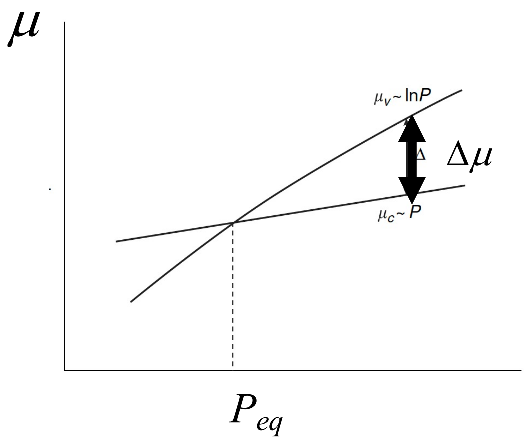
At given T and P, one defines the **supersaturation**

$$\Delta\mu(T,P) = \mu_v(T,P) - \mu_c(T,P)$$

$$= [\mu_v(T,P) - \mu_v(T,P_{eq})] - [\mu_c(T,P) - \mu_c(T,P_{eq})]$$

$$\simeq \int_{P_{eq}}^{P} \frac{\partial \mu_v}{\partial P}\, dP - \int_{P_{eq}}^{P} \frac{\partial \mu_c}{\partial P}\, dP = \int (v_v - v_c) dP \simeq \int v_v dP$$

$$\underline{\simeq k_B T \ln \frac{P}{P_{eq}}}$$ assuming an ideal gas



$$\Delta\mu \simeq k_B T \ln \frac{F}{F_{eq}}$$ with $F_{eq} = P_{eq}/\sqrt{2\pi m k_B T}$

$$\Delta\mu = 2.5\,\text{eV for Si at } T = 600\,\text{K with } P_{eq} = 1.3\,10^{-32}\,\text{atm and } F = 1\,\text{ML/s}$$

$$\Delta\mu = 1.2\,\text{eV for Si at } T = 1000\,\text{K}$$

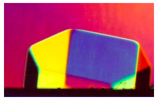
$$\Delta\mu = -0.2\,\text{eV for Si at } T = 1400\,\text{K}$$

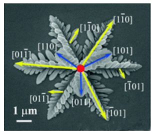
Growth from vapor
« very far »
from equilibrium
Cf Markov

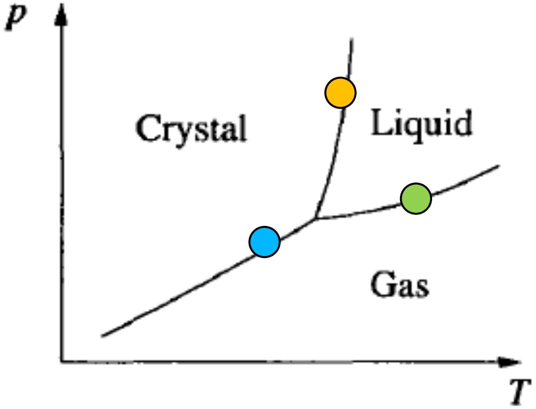
$$\Delta\mu_l = 0.003\,\text{eV for growth from liquid } \; T - T_{melt} = -10\,°\text{C}$$

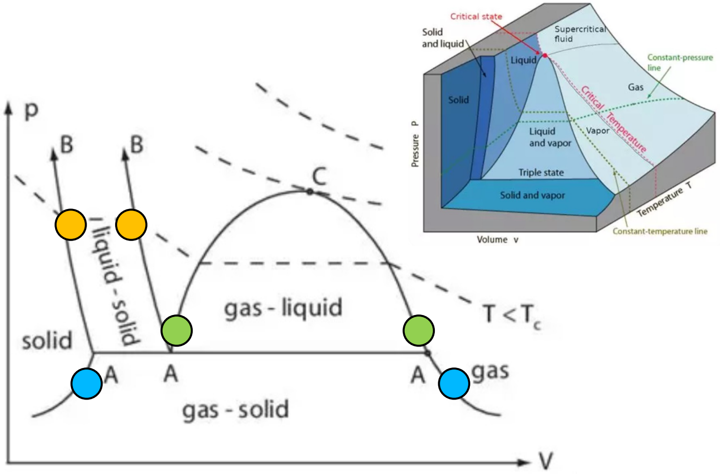
2. Phase separation

There can be an equilibrium
between **two** phases
with non-flat **interfaces**



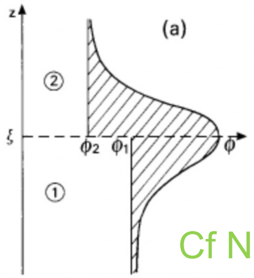






For a single phase, one has to minimize $G = U - T\,S + P\,V = \mu\,N$

For 2 phases, one needs to consider the « cost » of the interface
that is the excess quantity of the grand potential

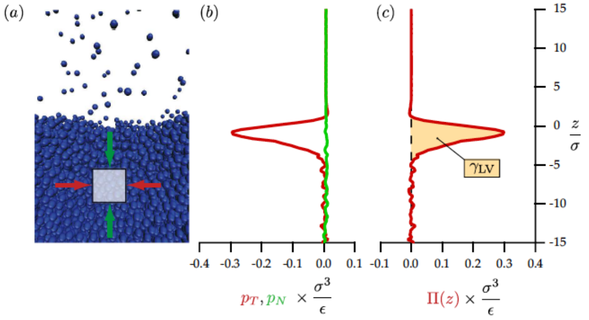


Cf Nozieres

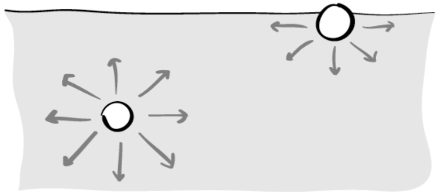
$$G_{tot} = \mu_1\,N_1 + \mu_2\,N_2 + \underline{\int \gamma\,dS}$$

Bulk quantities

Surface energy
=
Excess quantity

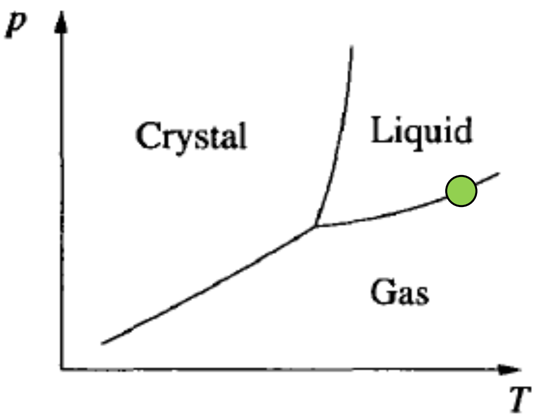


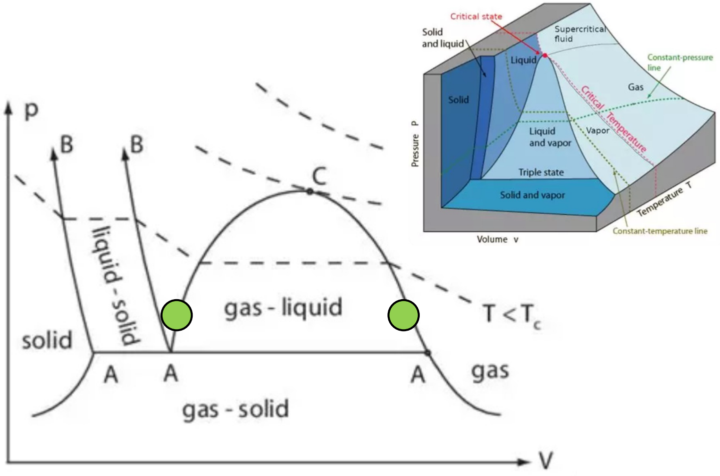
The surface energy γ can also be seen as
the « cost » of the broken bonds at the surface
(still with respect to the bulk case)



2. Phase separation

Liquid / gas coexistence
at given **total V and T**
for a **spherical** nucleus R



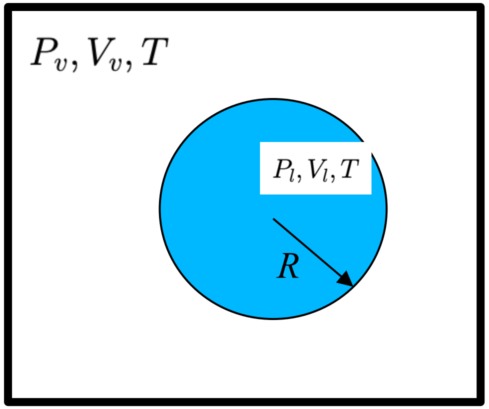


mechanical equilibrium

$$dF_{tot} = -P_v dV_v - P_l dV_l + \gamma dS$$

$$\underline{P_l - P_v} = \gamma \frac{dS}{dV_l} = \underline{\frac{2\gamma}{R}}$$

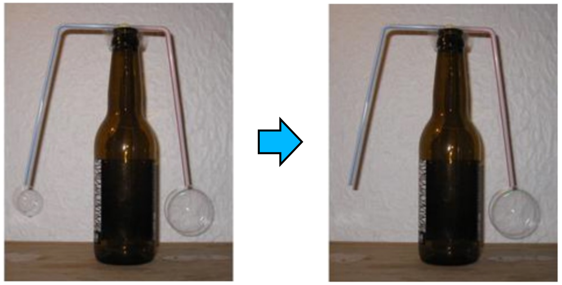
Laplace equation



More generally, with local curvatures

$$P_l - P_v = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

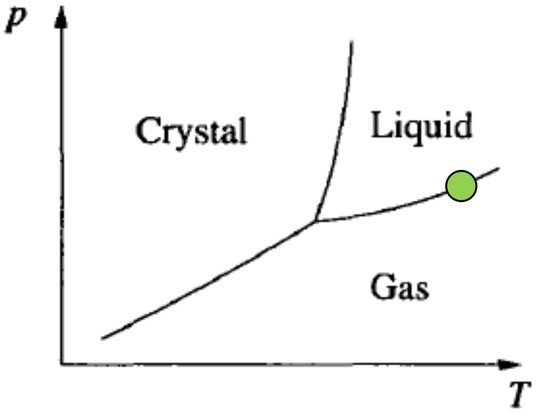
One finds typically $\Delta P = 1.5 \ \text{bar}$

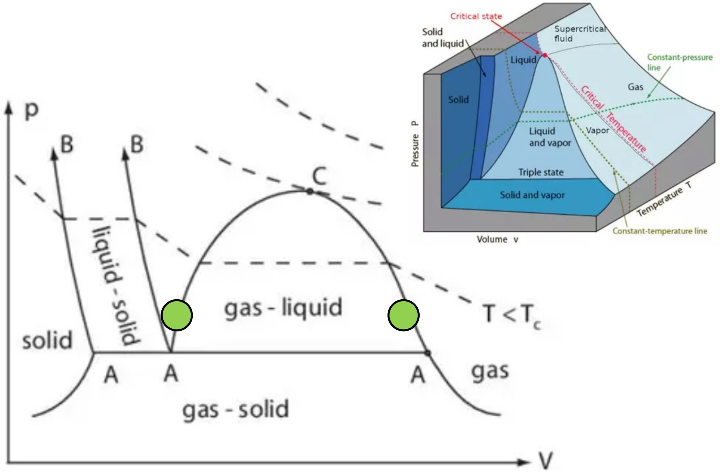


for a water droplet of 1 μm with $\gamma \sim 0.075\,\mathrm{J\,m^{-2}}$

2. Phase separation

Liquid / gas coexistence
at given P and T
for a spherical nucleus



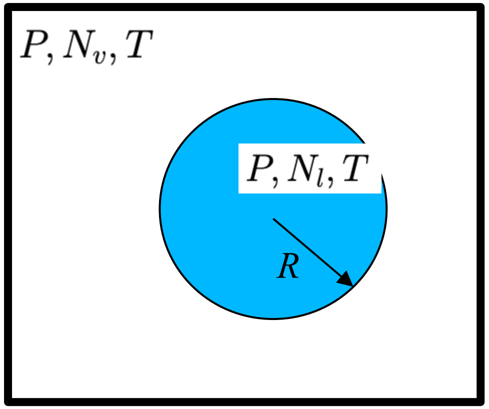


thermodynamic equilibrium

$$dG_{tot} = \mu_v\, dN_v + \mu_l\, dN_l + \gamma\, dS$$

⇨ $$\underline{\mu_v - \mu_l} = \gamma \frac{dS}{dN_l} = \underline{\frac{2\gamma\Omega}{r}}$$

Gibbs-Thomson equation
Ω atomic volume



$(\mu_v - \mu_l)\,\delta N = (P_l - P_v)\,\delta V$ is the work done to transfer δN particules from vapor to liquid

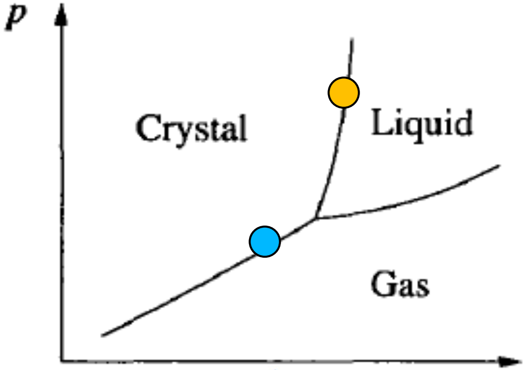
With $\Delta\mu(T,P) \simeq k_B T \ln \dfrac{P}{P_{eq}}$, one gets $P_{eq,R} = P_{eq,\infty} \exp\left(\dfrac{2\,\gamma\,\Omega}{R\,k_B T}\right)$

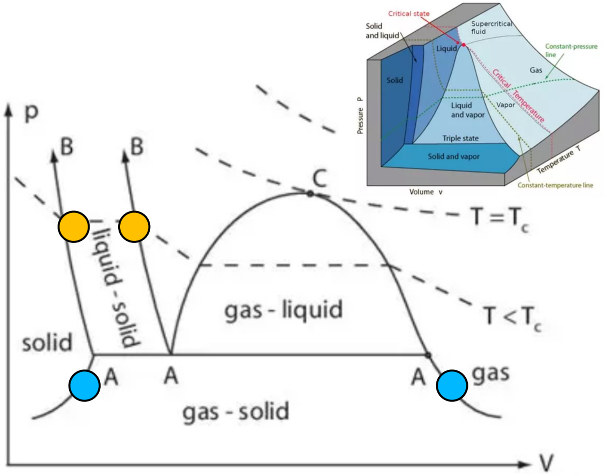
For a 1 μm water droplet, $P_{eq,R}/P_{eq,\infty} = 1.001$

For a 1 nm water droplet, ” 3.3

3. Equilibrium shape of crystals

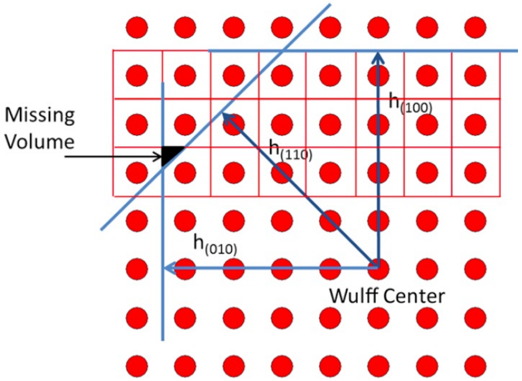
Crystal / fluid coexistence
at given V and T
for a crystalline nucleus





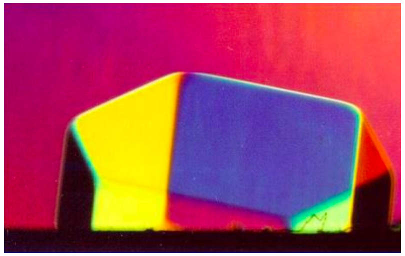
Anisotropy of the surface energy

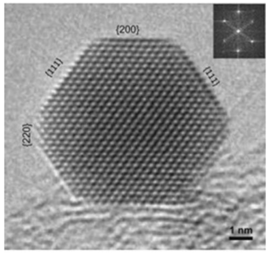
$$\gamma(\mathbf{n}) \quad \gamma(\theta,\phi) \quad \gamma(\theta)$$



The sphere no longer minimises the surface energy $\int \gamma(\mathbf{n})\, dS$ at given nucleus volume

Usually, crystals shapes are faceted





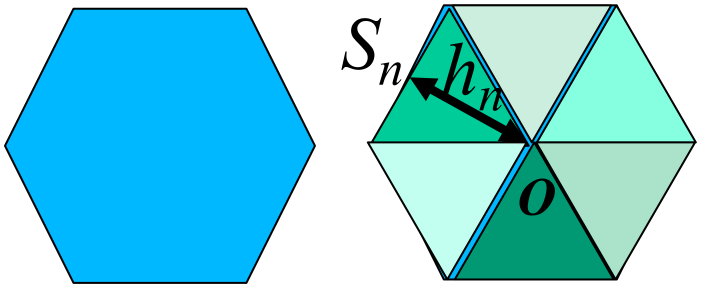
➡ What is the equilibrium shape of the crystal ??

3.a Gibbs - Curie - Wulff theorem

For a given V and T

$$dF_{tot} = -P_v\,dV_v - P_c\,dV_c + \sum_n \gamma_n dS_n$$
$$= -(P_c - P_v)\,dV_c + \sum_n \gamma_n dS_n = 0$$

We assume a polyhedron crystalline nucleus, made of pyramids with a common apex

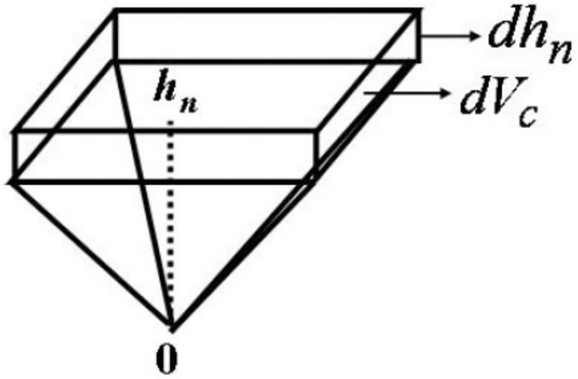


$$V_c = \frac{1}{3}\sum_n h_n\,S_n$$

$$\Rightarrow \quad dV_c = \frac{1}{3}\sum_n (S_n\,dh_n + h_n dS_n)$$

Up to first order $\quad dV_c = \sum_n S_n\,dh_n$

$$\Rightarrow \quad dV_c = \frac{1}{2}\sum_n h_n\,dS_n$$



$$\Rightarrow \quad \sum_n \left[\gamma_n - \frac{1}{2}(P_c - P_v)\,h_n\right] dS_n = 0$$

$$\Rightarrow \quad P_c - P_v = 2\frac{\gamma_n}{h_n}$$

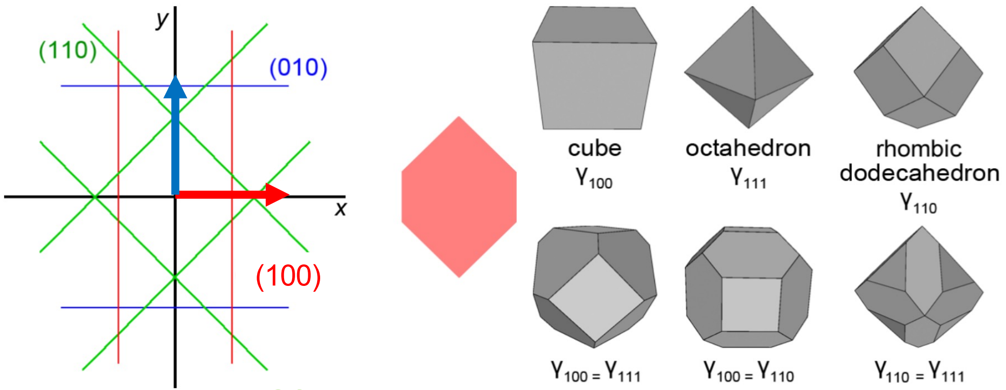
$$\frac{\gamma_n}{h_n} = cst$$

Gibbs - Curie – Wulff theorem

3.b Wulff construction

Polyhedra form $\frac{\gamma_n}{h_n} = cst$

> the distances of the crystal faces from a point within the crystal are proportional to the faces surface energies



Cf Barmparis

> - draw vectors normal to all possible crystallographic faces from an arbitrary point
> - distances proportional to the surface energies γ_n are marked on the vectors
> - planes normal to the vectors are constructed through the marks
> - the resulting closed polyhedron is the equilibrium shape

crystal faces which only touch the apexes of this polyhedron or are situated even further do not belong to the equilibrium form

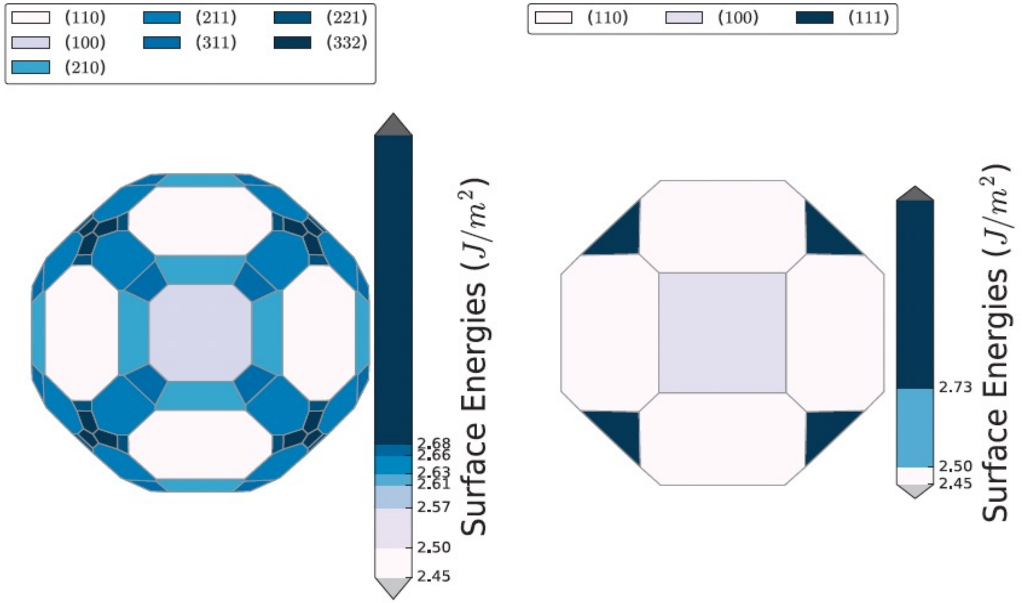
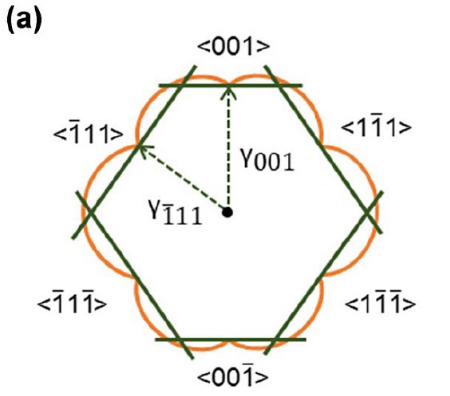
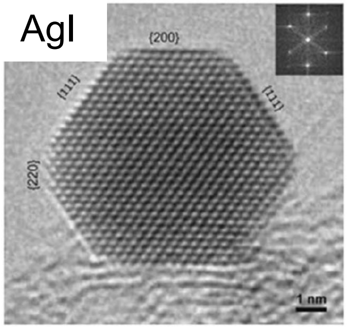


Figure 2. Wulff shape of Fe. The Wulff shape of α-Fe generated with surface energies for facets up to a max Miller index of (a) 3 and (b) 1.

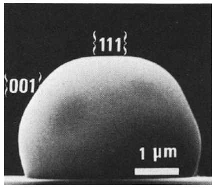
Cf Tran

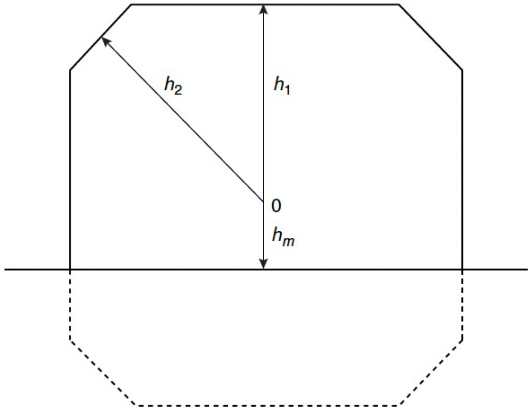




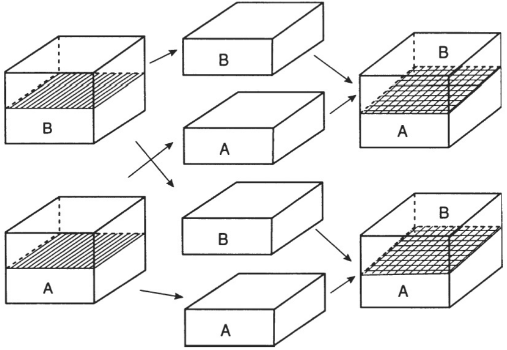
Cf Boukouvala 21

3.c Kaishew construction





Crystal in contact with a substrate



- consider the interfacial energy
  - to build 2 interfaces

$$2U_{int} = U_{AA} + U_{BB} - 2U_{AB}$$

  - with $\gamma_{hkl} = U_{hkl}/2S_{hkl}$

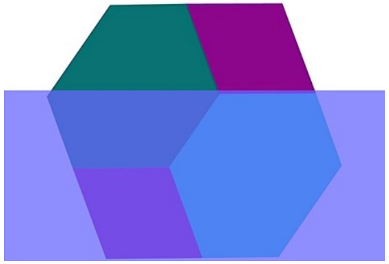
$$\gamma_{int} = U_{int}/S_{AB}$$

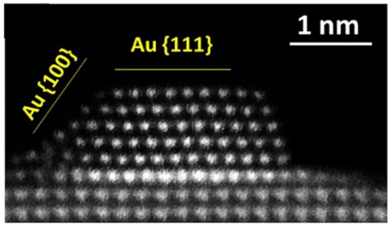
adhesion energy $\beta = U_{AB}/S_{AB}$

  - Duprey relation $\gamma_{int} = \gamma_A + \gamma_B - \beta$

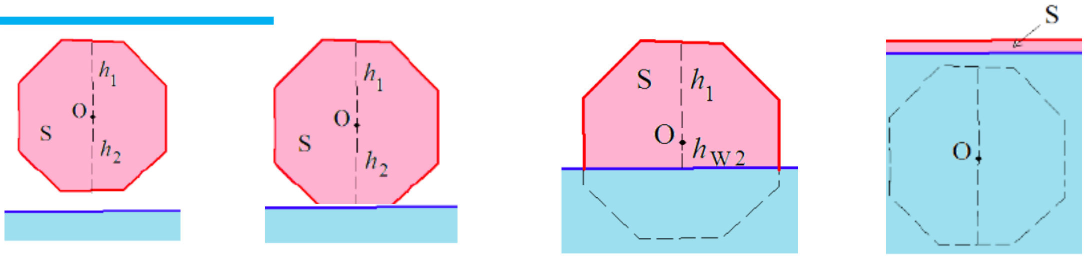
Equilibrium condition $dF = -P_v dV_v - P_c dV_c + \sum_{n \neq m} \gamma_n \, dS_n + (\gamma_{int} - \gamma_{sub}) \, dS_m = 0$

➡ $\dfrac{\gamma_n}{h_n} = \dfrac{\gamma_m - \beta}{h_m} = c^{st}$ Wulff-Kaishew theorem





Au/CeO$_2$



$\beta = 0$ $\beta = \gamma_{sub} + \gamma_m$ β

non-wetting

incomplete wetting

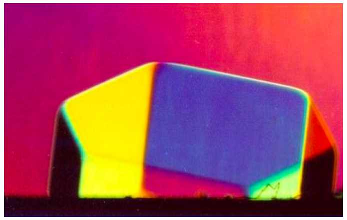
complete wetting

Cf Markov

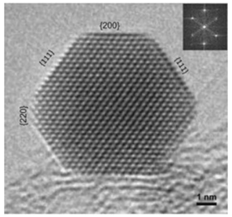
3.d Wulff today

Nanoparticles : size and shape matters
for their properties

cm

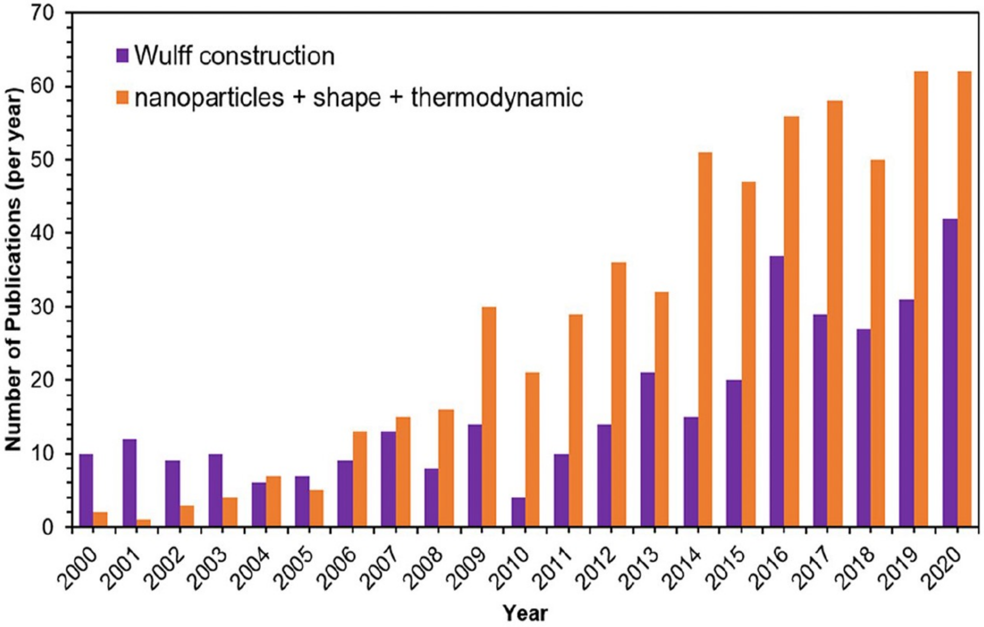


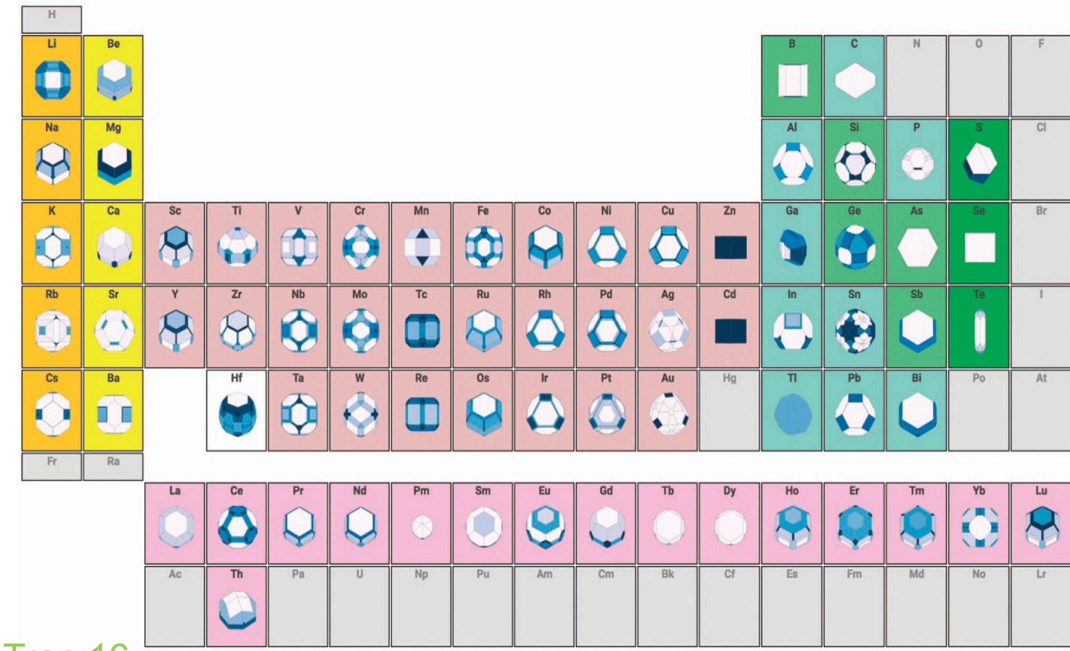
μm



nm

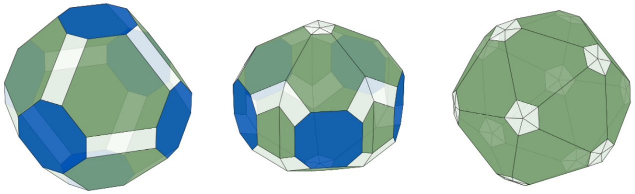
... renewed interest for the Wulff construction





Cf Tran 16

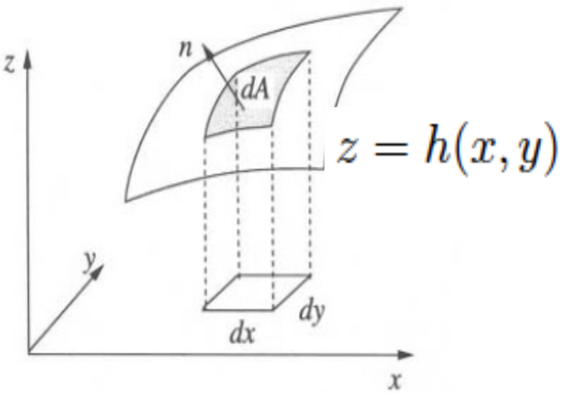
- ✓ self-contained packages for predicting crystal shapes



Cf WulffPack

- ✓ kinetic growth, alloys, supported nanoparticles, twinned crystals etc Cf Boukouvala 21

3.e Continuous shape



For a given P and T, crystal / gas coexistence for an arbitrary shape

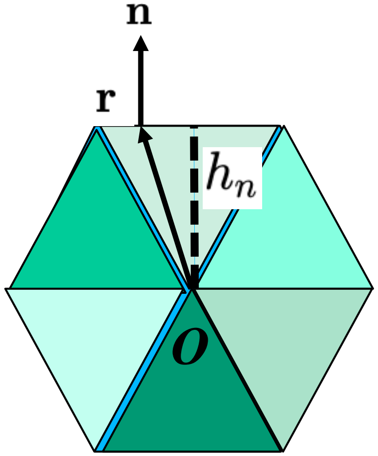
$$G[h(x,y)] = N_c\,\mu_c + N_l\,\mu_l + \int \gamma(\mathbf{n})\,dS$$

$$G^{vol} = -\frac{\Delta\mu}{v}\int h(x,y)\,dx\,dy + c^{st}$$

$$G^{surf} = \int \gamma(\mathbf{n})\sqrt{1+\nabla h^2}\,dx\,dy) \equiv \int f(h_x,h_y)\,dx\,dy$$

At equilibrium $\delta G = 0\,,\ \forall\ \delta h(x,y)$

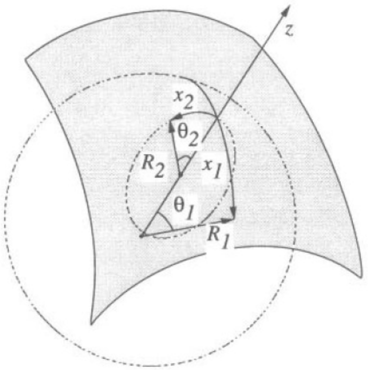
$$\begin{aligned}\delta G^{surf} &= \int dx\,dy\left[\frac{\partial f}{\partial h_x}\delta h_x + \frac{\partial f}{\partial h_y}\delta h_y\right]\\ &= -\int dx\,dy\,\delta h\left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial h_x}\right) + \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial h_y}\right)\right]\end{aligned}$$



The equilibrium solution satisfies $\frac{\partial f}{\partial h_x} = -\frac{\Delta\mu}{2\Omega}x$ idem for y

With the Legendre transformation, $g(x,y) = f - h_x\frac{\partial f}{\partial h_x} - h_y\frac{\partial f}{\partial h_y} = \frac{\Delta\mu}{2\Omega}h(x,y)$

➡ $\underline{\frac{2\Omega}{\Delta\mu}\gamma} = \frac{h - xh_x - yh_y}{\sqrt{1+\nabla h^2}} = \underline{\mathbf{r}\cdot\mathbf{n}}$ generalized Gibbs-Curie-Wulff theorem

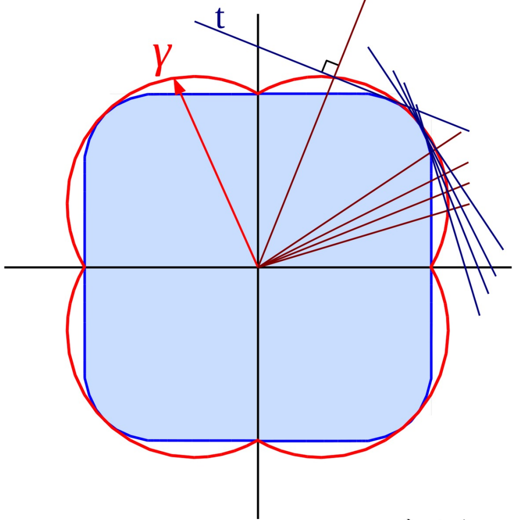


With the local approximate $z = -\frac{x_1^2}{2R_1} - \frac{x_2^2}{2R_2}$ and surface stiffness $\tilde{\gamma}_{ij} = \gamma\delta_{ij} + \frac{\partial^2\gamma}{\partial\theta_i\partial\theta_j}$

➡ $\underline{\frac{\Delta\mu}{\Omega} = \frac{\tilde{\gamma}_{11}}{R_1} + \frac{\tilde{\gamma}_{22}}{R_2}}$ Herring formula

Cf Saito

3.f Continous Wulff construction



Polyhedra form $\frac{2\Omega}{\Delta\mu}\gamma = \mathbf{r}\cdot\mathbf{n}$

- draw vectors normal to all possible directions
- mark distances proportional to the surface energies γ
- construct through the marks planes normal to the vectors
- the envelop of the perpendicular planes

gives the equilibrium shape

Ex : the 2d Ising model

$$\mathcal{H} = -\frac{J}{2}\sum_{\langle i,j\rangle} S_i\, S_j$$

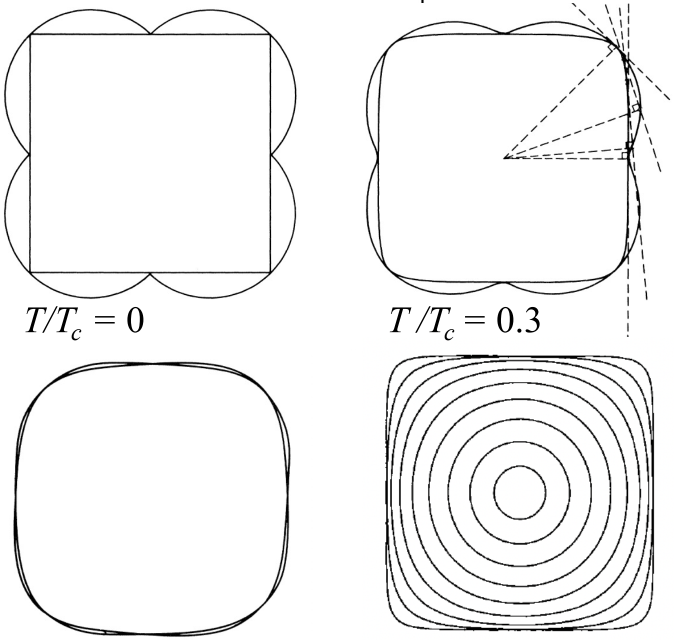
$$\frac{k_B T_c}{J} = \frac{1}{\ln(\sqrt{2}+1)}$$

cf Rottman

$$\gamma(\theta)/k_B T = \cos\theta\,|\,\sinh^{-1}(\alpha\,|\cos\theta\,|\,) + |\sin\theta\,|\sinh^{-1}(\alpha\,|\sin\theta\,|\,)$$

$$\alpha = \frac{2}{b}\left[\frac{1-b^2}{1+(\sin^2 2\theta + b^2\cos^2 2\theta)^{1/2}}\right]^{1/2}$$

$$b = \frac{2\sinh 2K}{\cosh^2 2K} \qquad \underline{K = J/k_B T}$$



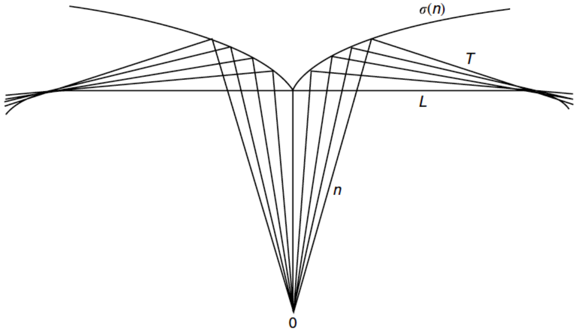
$T/T_c = 0$ $T/T_c = 0.3$

$T/T_c = 0.6$ $T/T_c = 0.1 \ldots 0.9$

cf Saito

Singular orientation give flat facets

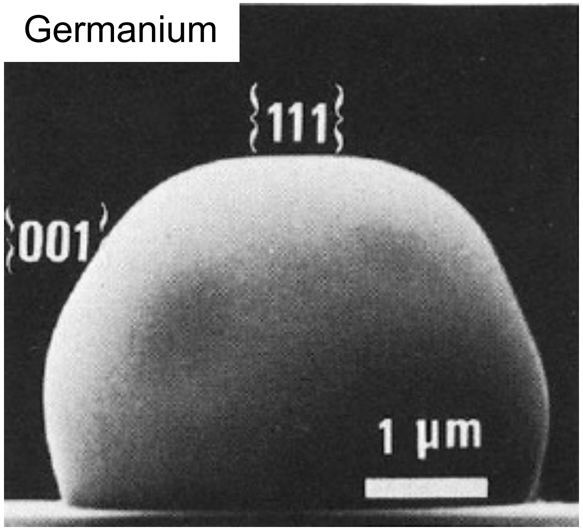
$$\frac{\Delta\mu}{\Omega} = \frac{\tilde{\gamma}_{11}}{R_1} + \frac{\tilde{\gamma}_{22}}{R_2}$$



3.g Inverse Wulff construction

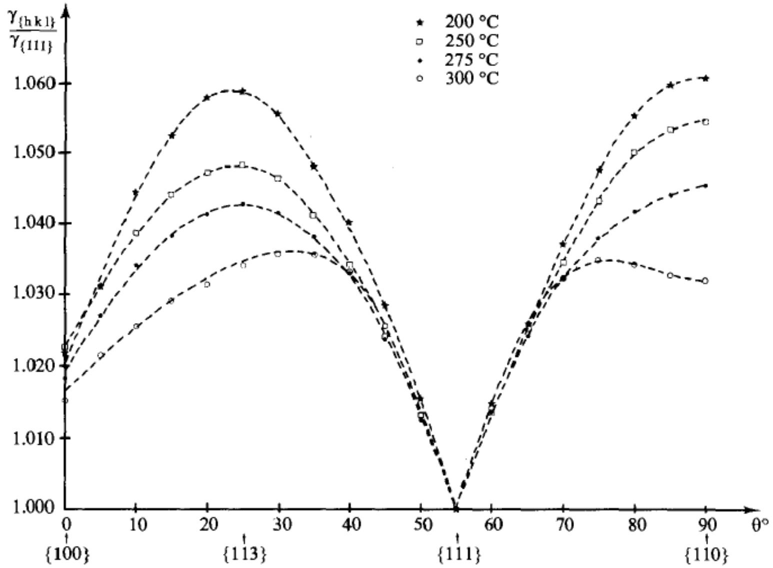
The correspondance between the crystal shape and surface energy allows to 'measure' surface energy ratios

Germanium

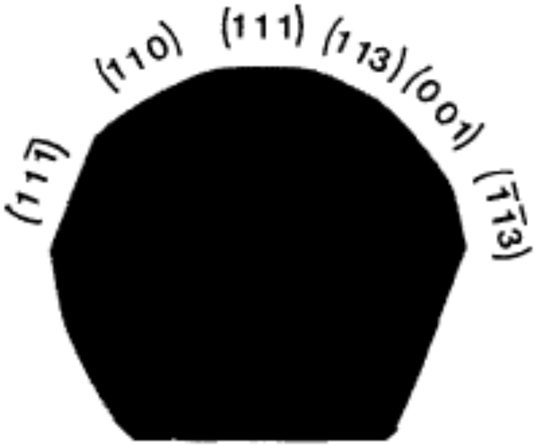


Cf Métois 87

↔

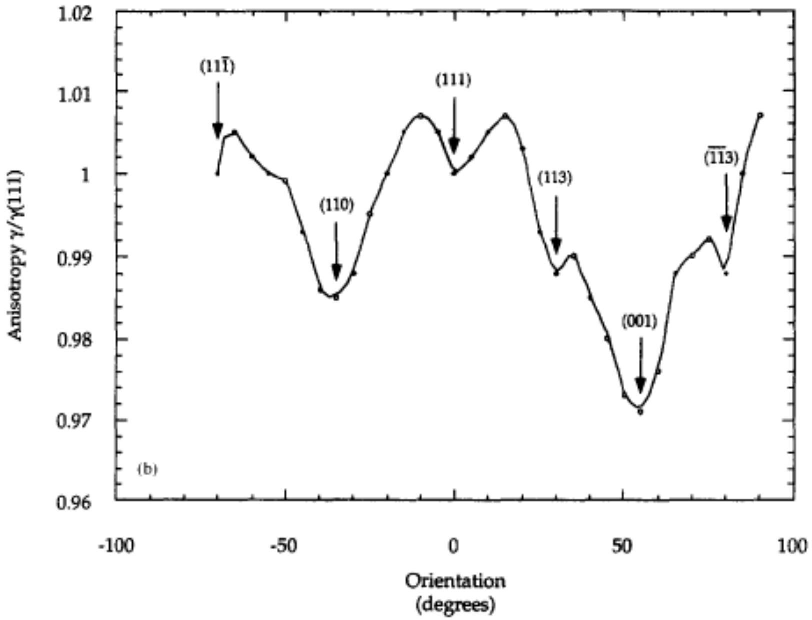


Silicium



Cf Bermond 95

↔



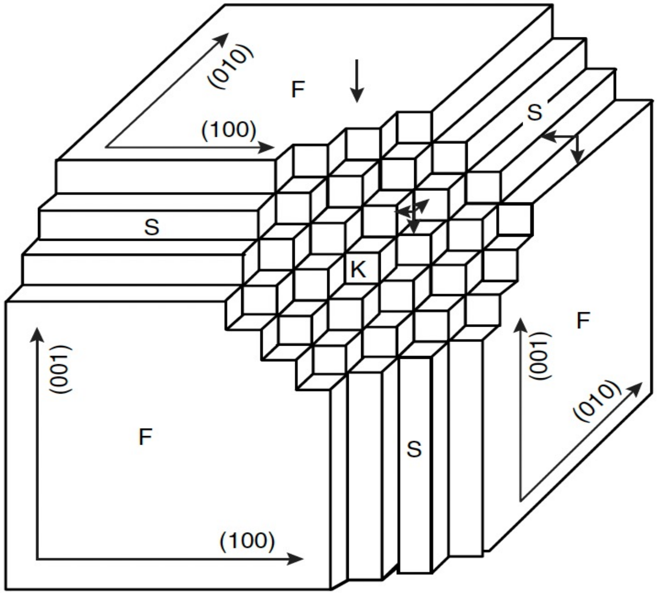
Crystals in and out of equilibrium

I. Crystal growth vs equilibrium

II. Equilibrium
  1. Phase transition
  2. Phase separation
  3. Equilibrium shape of crystals
    a. Gibbs-Curie-Wulff theorem
    b. Wulff construction
    c. Kaischew construction
    d. Wulff today
    e. Continuous shape
    f. Continuous Wulff construction
    g. Inverse Wulff construction
  4. Atomistic crystal shapes
  5. Step fluctuations on vicinal surfaces
  6. Roughening transition
    a. Jackson model
    b. Morphologies
    c. Mean-field approach
    d. Correlations
    e. Renormalisation group
    f. Experiments

III. Out-of-equilibrium properties
  1. Ideal laws
  2. Kinetic Wulf theorem
  3. Kinetics-limited growth
    a. Nucleation
    b. Step growth
    c. Noise induced roughening
    d. Growth under constraint
  4. Theoretical tools for epitaxy

4. Atomistic crystal shapes



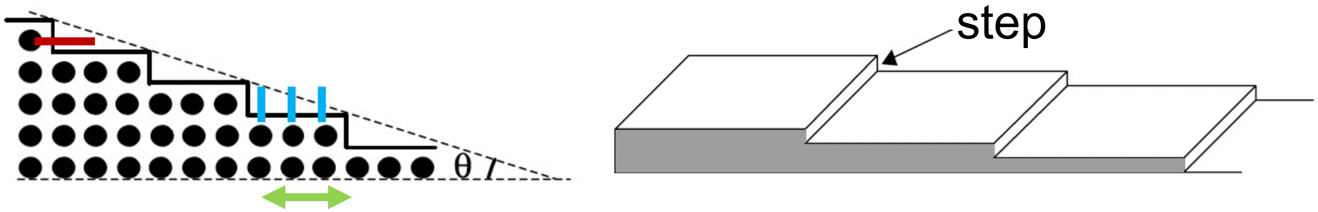
From an atomistic point of view, one can divide crystal surfaces in three groups

- ✓ F (flat) : parallel to at least 2 most dense rows of atoms
- ✓ S (stepped) : parallel to at most 1 dense rows of atoms
- ✓ K (kinked) : not parallel to any dense rows of atoms

For a cubic crystal, F : (001) ; S (110) ; K (111)

- Less broken bonds in F < S < K ... $\gamma_F < \gamma_S < \gamma_K$
- K faces offer more kink sites ... they grow faster than S faces ... that grow faster than F faces (for low enough supersaturation to prevent nucleation, F faces do not grow)

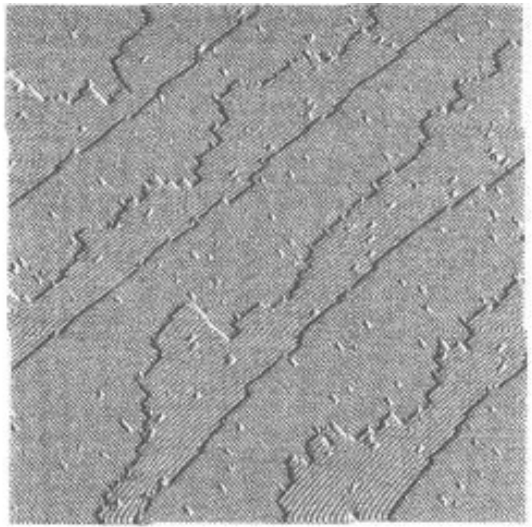
For a **vicinal** surface



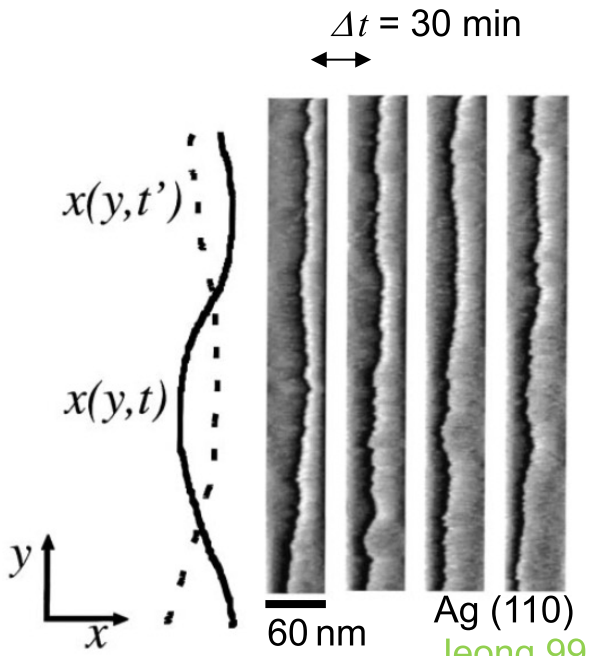
$$\frac{\gamma(\theta)}{|\cos\theta|} = \underline{\gamma_0} + \underline{(\beta_0/a)}|\tan\theta| + \underline{(\beta_2/a)}|\tan^3\theta|$$

5. Step fluctuations on vicinal surfaces

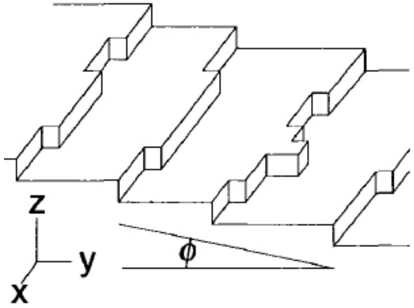
At equilibrium, atomic microscopy (AFM, STM, SEM...) reveals step fluctuations as a function of T.



Si (001)
Lagally 90



Ag (110)
Jeong 99



These step fluctuations allow to ‘measure’ step energetics.

Fluctuations are introduced thanks to the increase in entropy vs cost in energy

$$G = U - T\,S + P\,V$$

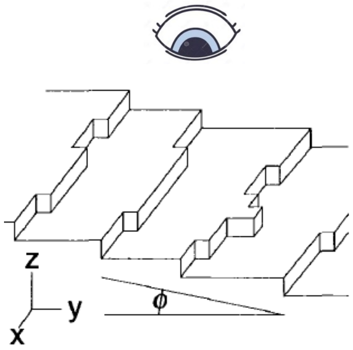
the balance between the two is a function of temperature

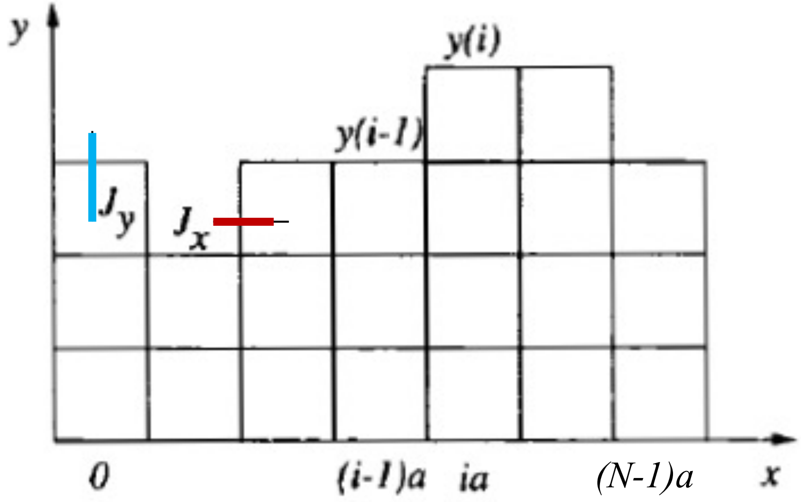
5. Step fluctuations on vicinal surfaces

Simple exact model of a step in 2D

$$\mathcal{H} = \underline{NJ_y} + \underline{J_x} \sum_{i=0}^{N-1} \frac{|y(i) - y(i+1)|}{a}$$

with $y(i) - y(i+1) \in \{0, \pm 1\}$





Cf Saito

$$\Rightarrow Z = \sum e^{-\beta\mathcal{H}}$$

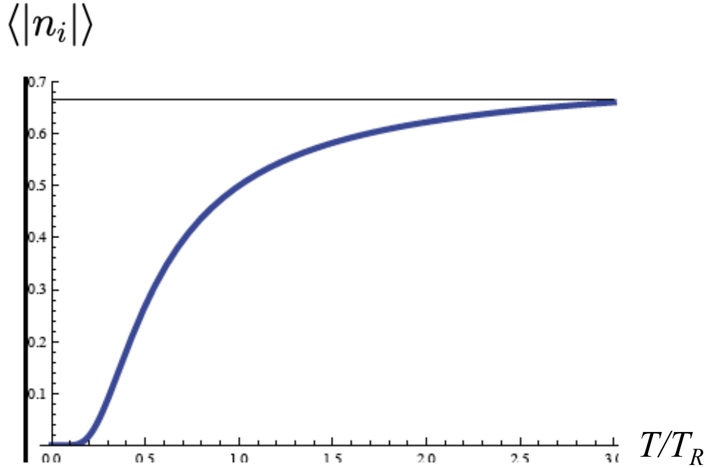
$$= e^{-\beta N J_y} \sum_{n_i = 0, \pm 1} \prod_i e^{-\beta J_x |n_i|}$$

$$= e^{-\beta N J_y} \left(1 + 2e^{-\beta J_x}\right)^N$$

$$\Rightarrow F_{kink} = -k_B T \log Z \propto J_y - k_B T \log(1 + 2e^{-\beta J_x})$$

$$\Rightarrow \langle |n_i| \rangle = \frac{2\exp(-J_x/k_B T)}{1 + 2\exp(-J_x/k_B T)}$$

finite density of kinks at equilibrium



When $J_x = J_y$, $\underline{F_{kink} = 0}$ at $\underline{T_R = \frac{J}{k_B \log 2}}$

entropy-induced kink creation !

The kink density is continous, as all its derivative at T_R $\langle |n_i| \rangle = \frac{1}{1 + e^{(1/T - 1/T_R)J/k_B}}$

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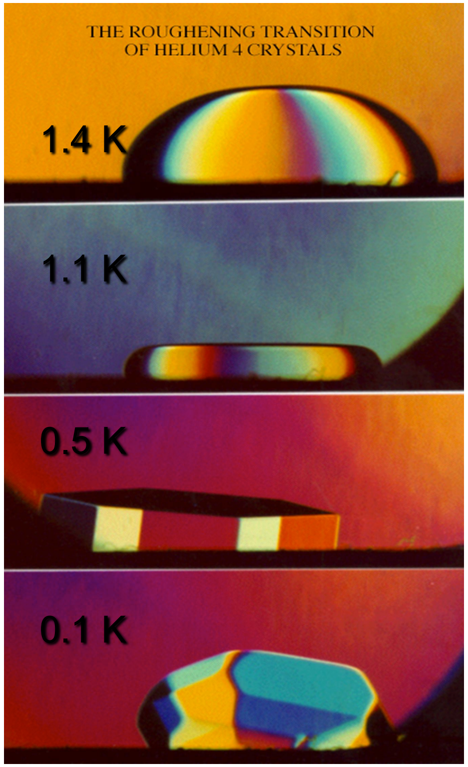
6. Roughening transition

- The roughening transition occurs when a crystalline interface changes from a smooth to a rough state at some temperature T_R

$T < T_R$ the surface is made of flat facets
$T > T_R$ the surface is rough and may be curved

This transition is a smooth, infinite order transition !

It is belongs to the Berezinskii - Kosterlitz - Thouless universality class

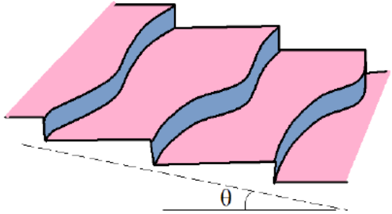


^{4}He Balibar 05

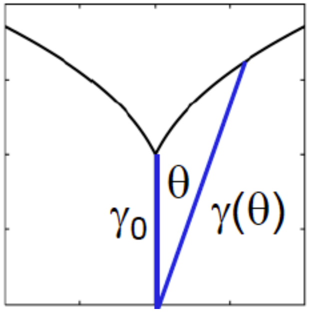
First demonstrated for vicinal surfaces by Burton-Cabrera-Franck

$$\frac{\gamma(\theta)}{|\cos\theta|} = \gamma_0 + (\beta_0/a)|\tan\theta| + (\beta_2/a)|\tan^3\theta|$$

step energy



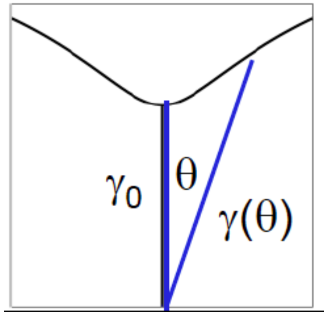
$\beta_0 \neq 0 \quad \gamma(\theta) \simeq \gamma_0 + \beta_0/a|\theta| + \mathcal{O}(\theta^2)$



Cusp singularity in γ

⇨ facet with a size $\sim \beta_0$

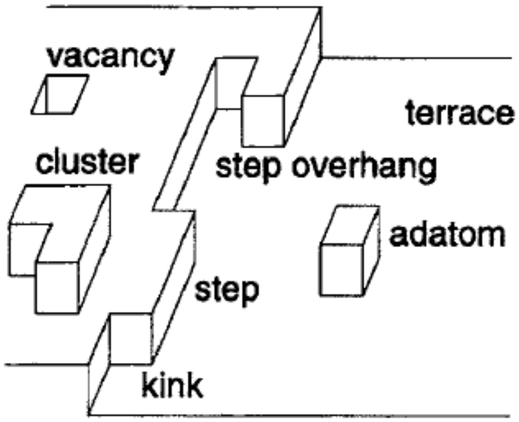
$\beta_0 = 0 \quad \gamma(\theta) \simeq \gamma_0 + \gamma_2\theta^2 + \mathcal{O}(\theta^3)$



No singularity in γ

⇨ no facet in the equilibrium shape

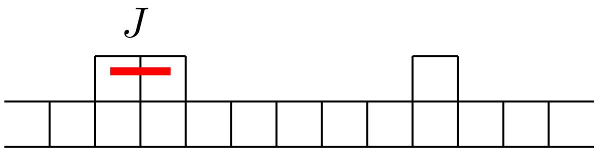
6.a Jackson model



Simplify model :

- ✓ the interface is made of a **single** layer, divided into a 2D lattice, where each site is either occupied or empty
- ✓ each of the N sites has z_s neighbor sites
- ✓ cohesive energy J between neighboring crystal atoms

The broken bond Hamiltonian



$$\mathcal{H} = J\sum_{\langle ij\rangle}[\, n_i(1-n_j) + (1-n_i)n_j] + \Delta\mu\sum_i n_i$$

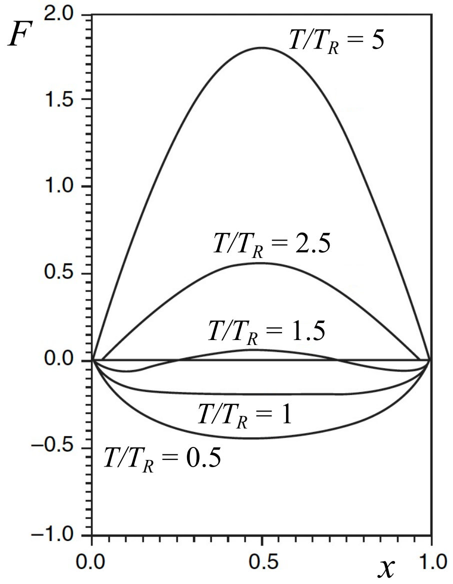
with $n_i = 0, 1$, is equivalent to the Ising model $\mathcal{H} = -\frac{J}{2}\sum_{\langle ij\rangle} S_i S_j - H\sum_i S_i$ with $S_i = +1, -1$, $H = \Delta\mu/2$
... there exists a phase transition

Mean-field treatment $E_{coh} = z_s J N_s(1 - N_s/N)$ where N_s is the number of atoms

There are $\Omega = \binom{N}{N_s}$ possible states and $S = k_B \log\Omega$

$$\ldots F = E - T\,S = JNz_s\left[x(1-x) + \frac{T}{2T_R}\left(x\log x + (1-x)\log(1-x)\right)\right]$$

with $x = N_s/N \;\&\; T_R = Jz_s/2k_B$

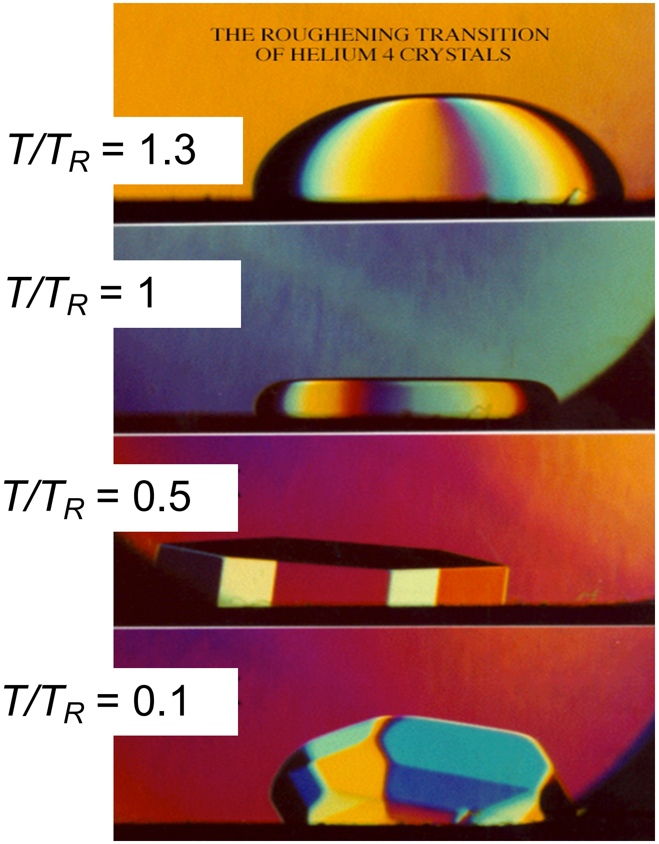


➡ $T < T_R$ $x \simeq 1/2$ rough interface

$T > T_R$ $x \simeq 0$ ou 1 smooth face

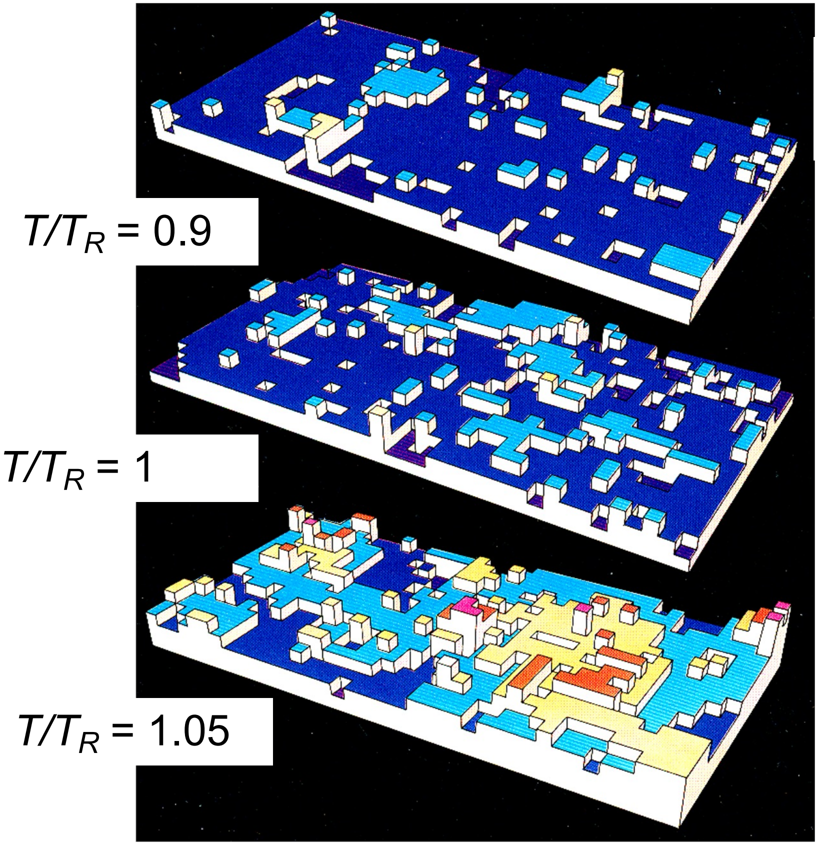
6.b Morphologies

experiments on ^{4}He



Balibar 05

Monte-Carlo simulations of the SOS model



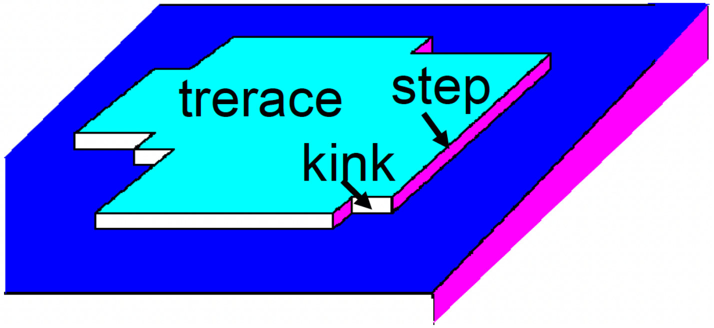
Leamy 74

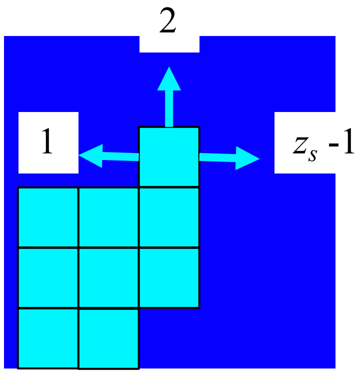
$$\mathcal{H} = J \sum_{\langle ij \rangle} |h_i - h_j| + \Delta\mu \sum_i h_i$$

$k_B\, T_R / 2\ \mathrm{J} = 0.632\, J$

6.c Mean-field approach

Crude estimate of the free energy cost to create a monolayer island

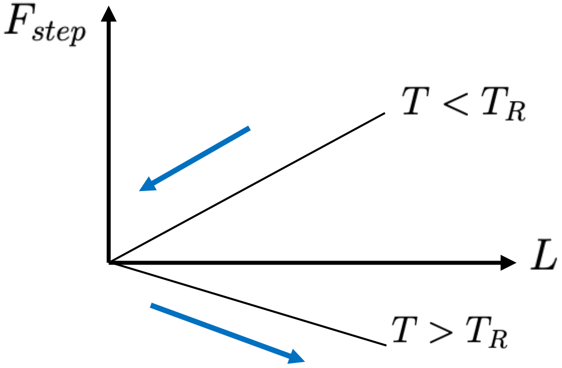




Consider an island enclosed by a step loop of length L

$$E_{step}(L) \sim J\frac{L}{a} \qquad S_{step} = k_B \ln\Omega \sim k_B \ln(z_s - 1)^{L/a}$$

$$\Rightarrow F_{step} = [J - k_B T \ln(z_s - 1)](L/a) = \beta_0(L)L$$

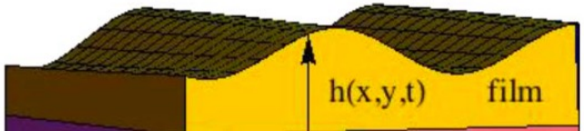


At $T_R = J/k_B \ln(z_s - 1)$, the step free energy vanishes $\beta_0 = 0$

✓ $T < T_R, \beta_0 > 0$, F is minimum at $L=0$, no island, flat

✓ $T > T_R, \beta_0 < 0$, F is minimum at $L = \infty$, many islands, rough

6.d Correlations



For a rough continuum surface (above T_R) :

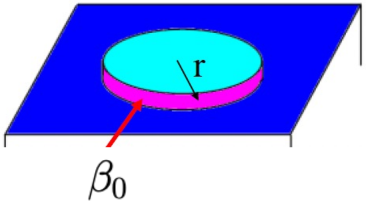
$$F^{surf} = \frac{1}{2}\int d\mathbf{r}\,\tilde{\gamma}(0)[\nabla h(\mathbf{r})]^2 = \frac{1}{2}\int \frac{d\mathbf{k}}{(2\pi)^2}\tilde{\gamma}(0)k^2|h(\mathbf{k})|^2 \quad \Rightarrow \quad |h(\boldsymbol{k})|^2 = \frac{k_BT}{\tilde{\gamma}k^2} \quad \text{(equipartition)}$$

$$\Rightarrow \quad G(\boldsymbol{r}) = 2\int \frac{d\boldsymbol{k}}{(2\pi)^2}\langle|h(\boldsymbol{k})|^2\rangle(1-\cos\boldsymbol{k}\cdot\boldsymbol{r}) \sim \int_{1/r}^{\pi/a}\frac{kdk}{\pi}\frac{k_BT}{\tilde{\gamma}k^2}$$

$$G(\boldsymbol{r}) \sim \frac{k_BT}{\pi\tilde{\gamma}}\ln(r/a) + c^{st} \underset{r\to\infty}{\rightarrow} \infty$$

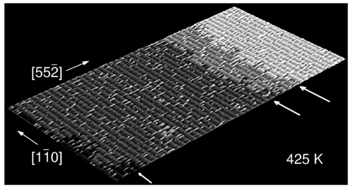
$$\Rightarrow \quad \langle h^2\rangle = \frac{k_BT}{2\pi\tilde{\gamma}}\ln(L/a)$$

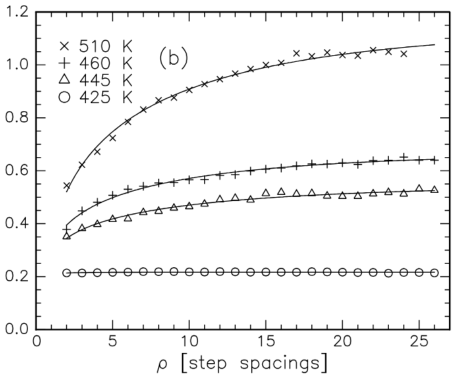
On a flat surface (below T_R), an island free energy is $\Delta F = 2\pi\, r\, \beta_0$

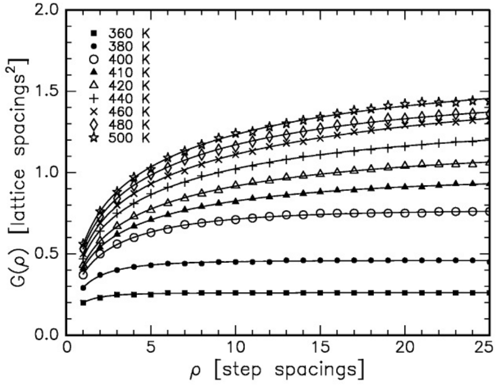


$\Rightarrow$ Small islands $r \leq \xi = k_BT/\beta_0$ are thermally excited

- ✓ between two points separated by $r \leq \xi$, heights behave like on a rough surface $G(r) \sim \ln r$
- ✓ Fo $r \geq \xi$, islands are separated, G(r) should saturate $G(r) \sim \ln \xi$







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Hoogeman 99

Hoogeman 00

6.e Renormalisation group

$$\mathcal{H} = \frac{1}{2}\int d\mathbf{r}\,[\tilde{\gamma}(0)(\nabla h)^2 + V\cos(\tfrac{2\pi z}{a})]$$

For a rough interface with a crystallographic potential

$$\langle\cos(2\pi h/a)\rangle \sim \left\langle 1 - \tfrac{1}{2}\left(\tfrac{2\pi h}{a}\right)^2\right\rangle \sim \exp\left(-2\pi^2\frac{\langle h^2\rangle}{a^2}\right)$$

scaling analysis $\langle V\rangle \sim VL^2\exp\left(-2\pi^2\frac{\langle h^2\rangle}{a^2}\right) \sim VL^{2-\pi k_BT/\tilde{\gamma}a^2}$

If $T > T_R \equiv 2\tilde{\gamma}a^2/\pi k_B$, the crystallographic potential vanishes during renormalization ...
behaves as before with $G(r) \sim \ln r$ at large r : rough surface

If $T < T_R$, the potential diverges upon coarse-graining ...
the surface is pinned to the crystallographic orientation, $G(r) \sim \ln\xi$ at large r : flat surface

The correlation length is $\xi \sim e^{\frac{c}{\sqrt{T_R - T}}}$

At T_R, the line energy vanishes as k_BT/ξ , as do all its derivatives !

- ✓ infinite order transition, in the universality class as Berezinskii-Kosterlitz-Thouless transition
- ✓ no order parameter, no symmetry breaking
- ✓ no singularity at the transition, no latent heat

Analogous to the phase transition in

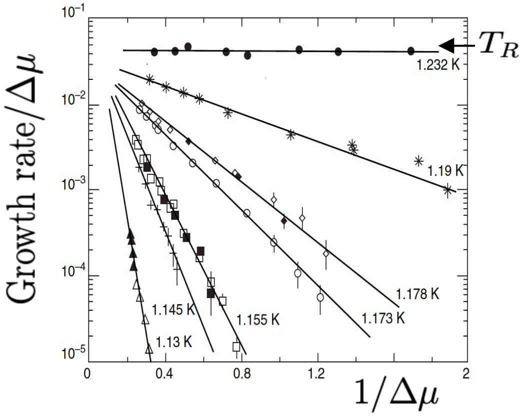
- superfluid/normal fluid
- superconductor/metal
- conductor/isolator in 2D charged fluids
- XY model of ferromagnet

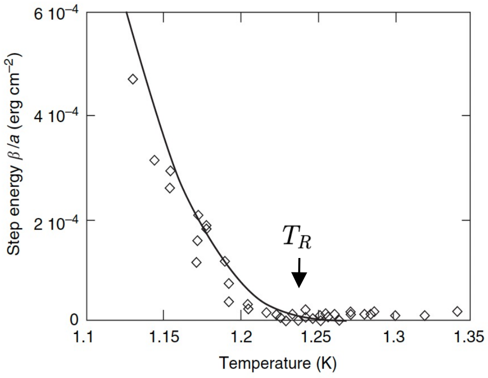
6.f Experiments

Above T_R, the interface is rough,
the growth rate is linear in $\Delta\mu$

Below T_R, $V \propto \Delta\mu \exp(-K_2/\Delta\mu)$

At T_R, the step ener energy vanishes $\sim e^{-\frac{c}{\sqrt{T_R - T}}}$

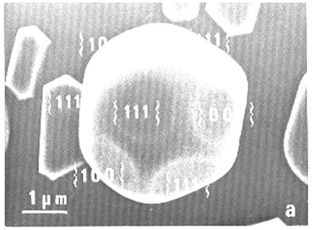




^{4}He

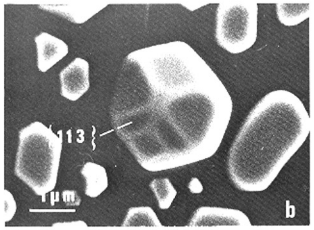
Balibar 05

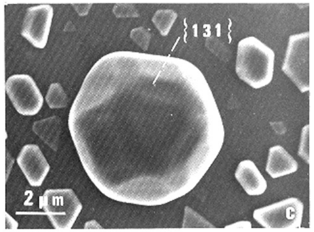
Indium



$T > 100$ °C

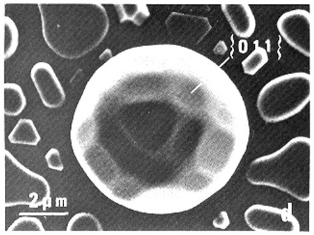
40 °C $< T <$ 100 °C

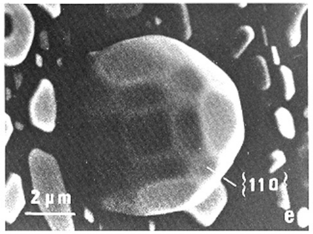




20 °C $< T <$ 40 °C

10 °C $< T <$ 20 °C



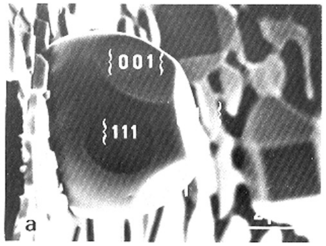


10 °C $< T <$ 20 °C

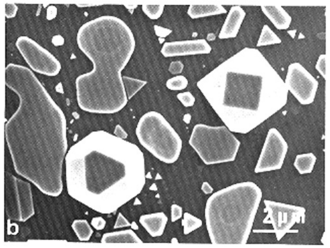
Heyraud 87

Pb

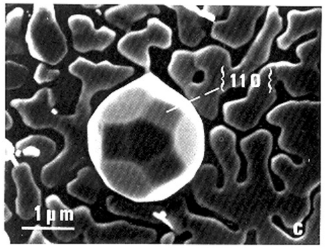
T > 120 °C



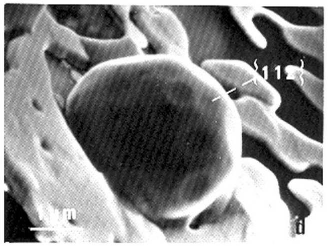
T > 120 °C



50 °C < T < 120 °C



T < 50 °C



Silicium : (110) $T_R = 1340$ °C ; (113) $T_R = 1370$ °C ; (111) no transition up to 1400 °C ; (001) always rough Heyraud 99

Crystals in and out of equilibrium

I. Crystal growth vs equilibrium

II. Equilibrium
   1. Phase transition
   2. Phase separation
   3. Equilibrium shape of crystals
      a. Gibbs-Curie-Wulff theorem
      b. Wulff construction
      c. Kaischew construction
      d. Wulff today
      e. Continuous shape
      f. Continuous Wulff construction
      g. Inverse Wulff construction
   4. Atomistic crystal shapes
   5. Step fluctuations on vicinal surfaces
   6. Roughening transition
      a. Jackson model
      b. Morphologies
      c. Mean-field approach
      d. Correlations
      e. Renormalisation group
      f. Experiments

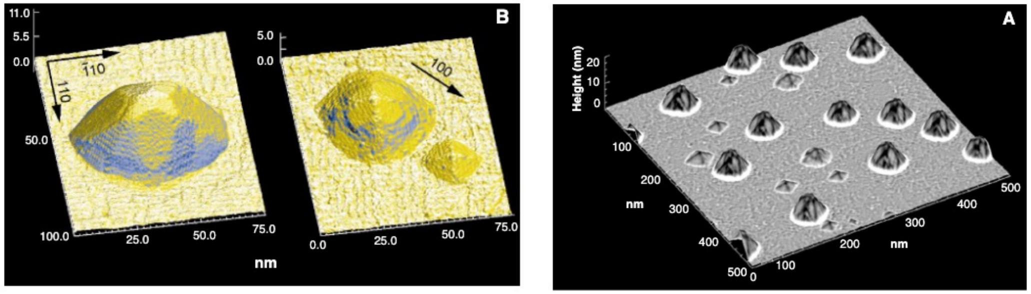
III. Out-of-equilibrium properties
   1. Ideal laws
   2. Kinetic Wulf theorem
   3. Kinetics-limited growth
      a. Nucleation
      b. Step growth
      c. Noise induced roughening
      d. Growth under constraint
   4. Theoretical tools for epitaxy

III. Out-of-Equilibrium

1. Ideal laws

Ge growth on Si(001)

Ge equilibrium shape



Cf Medeiros 98

$\neq$

Cf Tran 16

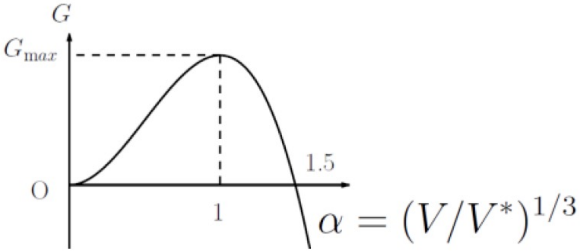
… need for the description of growth

Energy barrier for nucleation of a nanocrystal $\Delta G = -\Delta\mu \frac{V}{\Omega} + \sum_n \gamma_n S_n$ & $\frac{\gamma_n}{h_n^*} = \frac{\Delta\mu}{2\Omega}$

For a dilatation $h_n = \alpha h_n^*,\ S_n = \alpha^2 S_n^*,\ V = \alpha^3 V^*$

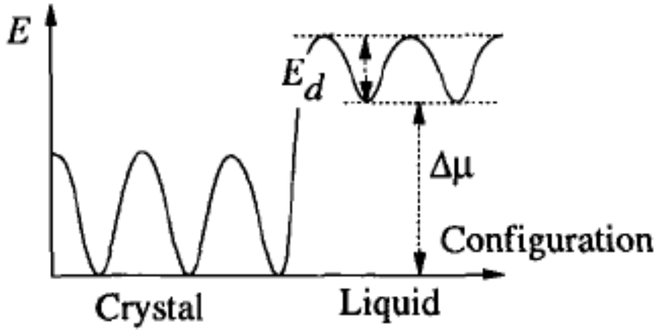
…. $G = G_{max}(3\alpha^2 - 2\alpha^3)$ with $G_{max} = \frac{\Delta\mu}{2\Omega} V^*$

with thermal fluctuations



> a nucleus with $V < V^*$ melts back
>
> a nucleus with $V > V^*$ grows

1. Ideal laws



For a **supercooled liquid** :

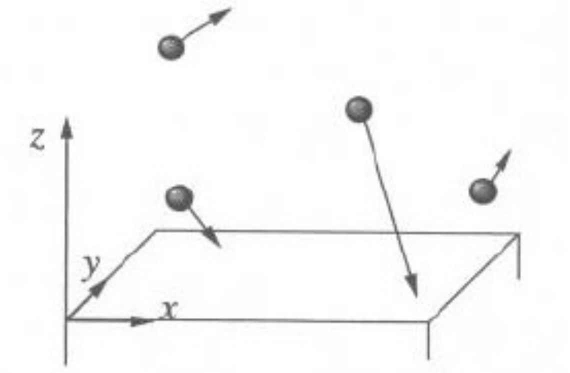
- atomic vibrations $\nu \sim 10^{13}\,\mathrm{s}^{-1}$
- liquid --> crystal events $\nu e^{-\beta E_d}$
- crystal --> liquid events $\nu e^{-\beta(E_d+\Delta\mu)}$

The crystallisation front advances at the speed $v = a\nu\left[e^{\beta E_d} - e^{-\beta(E_d+\Delta\mu)}\right]$

➡ The growth rate is $v = K\left[1 - e^{-\beta\Delta\mu}\right]$ Wilson-Frenkel ideal law for growth from a liquid

For small undercooling $\Delta\mu = \dfrac{l}{T_M}\Delta T$, linear dependance $v = K_T \Delta T$

1. Ideal laws



Growth from **vapor**

- velocity distribution in a perfect gas $\rho(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\beta \frac{1}{2} m \mathbf{v}^2\right)$
- during dt, $\int dv_x\, dv_y \int_{-\infty}^{0} dv_z\, \rho(\mathbf{v}) S v_z dt\, n = S\, dt \sqrt{\frac{k_B T}{2\pi m}} n$ particles hit the surface
- assuming perfect sticking, adsorption enforces the advance of the crystallisation front by $v_+ = a\, a^2 dt \frac{P}{\sqrt{2\pi m k_B T}}$
- desorption balances adsorption at saturation vapour pressure $v_- = -a\, a^2 dt \frac{P_{eq}}{\sqrt{2\pi m k_B T}}$

Ideally, the growth rate for growth from a gas $v = \frac{a^3}{\sqrt{2\pi m k_B T}}(P - P_{eq})$ Hertz-Knudsen law

For an ideal gas, $\Delta\mu \simeq k_B T \ln \frac{P}{P_{eq}}$

➡ $v = K(e^{\beta\Delta\mu} - 1) \approx \beta K \Delta\mu$ ideal law (rough interface, no transport issue in the gas …)

$$K = \frac{\Omega P_{eq}}{\sqrt{2\pi m k_B T}}$$

2. Kinetic Wulff theorem

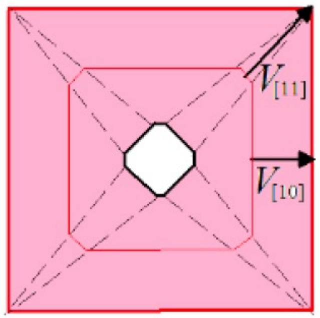
According to the ideal laws, but also to the linear response theory $V(\boldsymbol{n}) = K(\boldsymbol{n})\,\Delta\mu$

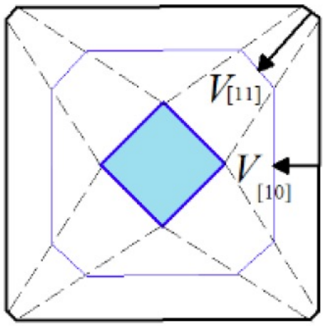
For a facet with given orientation, $h(\boldsymbol{n}) = \boldsymbol{r}\cdot\boldsymbol{n} = \int_0^t dt\,V(\boldsymbol{n}) = V(\boldsymbol{n})\,t = K(\boldsymbol{n})\Delta\mu\,t$

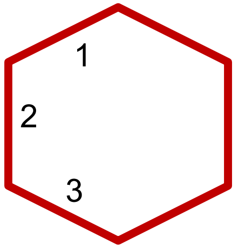
➡ kinetic Wulff theorem $\frac{K(\boldsymbol{n})}{h(\boldsymbol{n})} = \frac{1}{\Delta\mu\,t} = c^{st}$

similar to the equilibrium Wulff theorem $\frac{\gamma(\boldsymbol{n})}{h(\boldsymbol{n})} = \frac{\Delta\mu}{2\Omega}$

- ✓ Growth shapes are dominated by the slowest faces
- ✓ Melting shapes are dominated by the fastest faces







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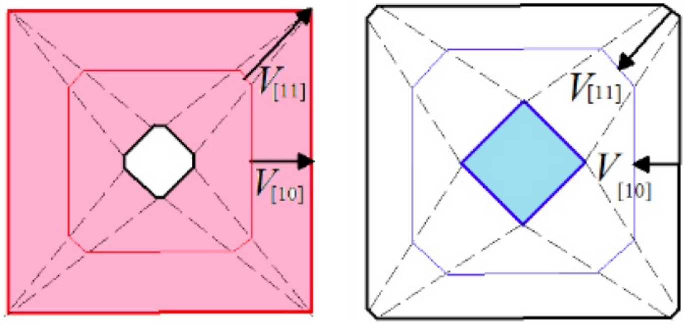

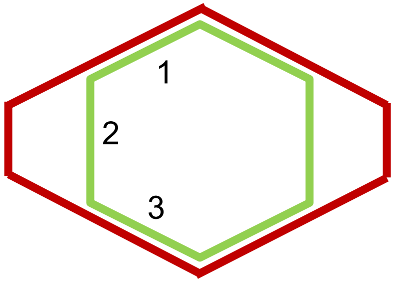

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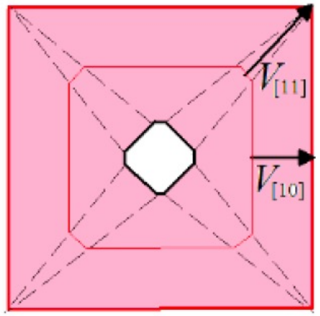

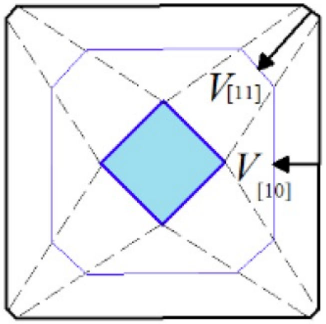

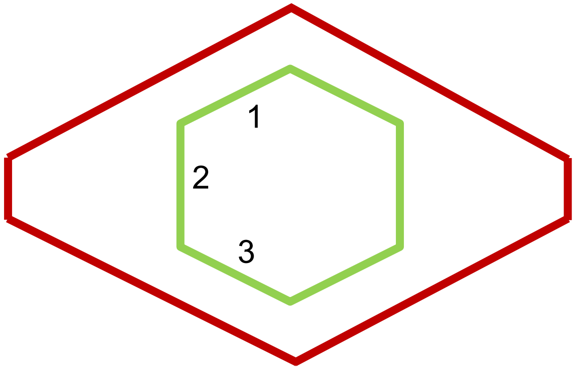

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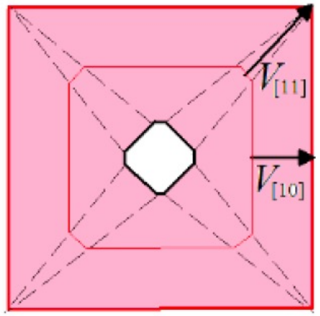

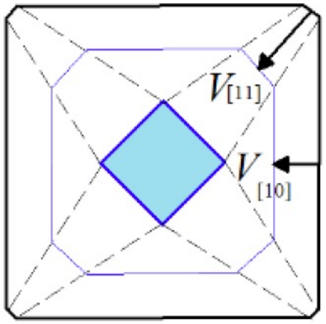

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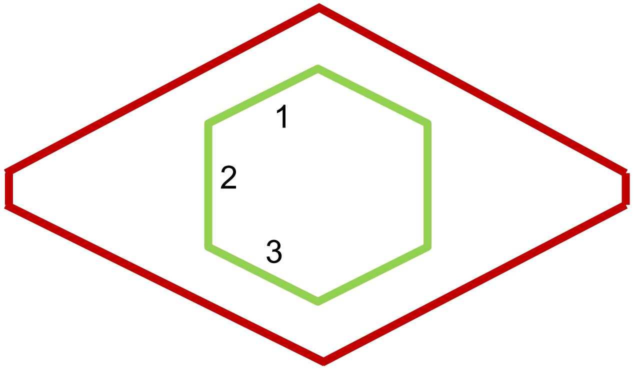

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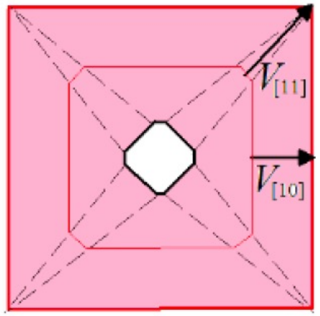
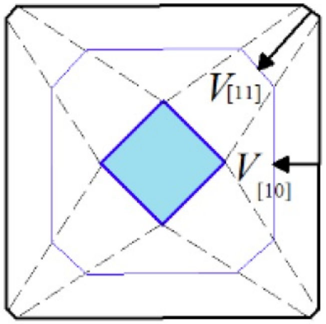
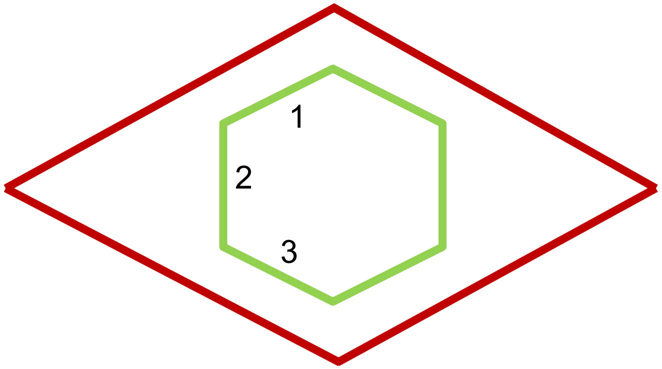




➡ kinetic Wulff theorem $\dfrac{K(\boldsymbol{n})}{h(\boldsymbol{n})} = \dfrac{1}{\Delta\mu\,t} = c^{st}$

similar to the equilibrium Wulff theorem $\dfrac{\gamma(\boldsymbol{n})}{h(\boldsymbol{n})} = \dfrac{\Delta\mu}{2\Omega}$

- ✓ Growth shapes are dominated by the slowest faces
- ✓ Melting shapes are dominated by the fastest faces



2. Kinetic Wulff theorem

According to the ideal laws, but also to the linear response theory $V(\boldsymbol{n}) = K(\boldsymbol{n})\,\Delta\mu$

For a facet with given orientation, $h(\boldsymbol{n}) = \boldsymbol{r}\cdot\boldsymbol{n} = \int_0^t dt\,V(\boldsymbol{n}) = V(\boldsymbol{n})\,t = K(\boldsymbol{n})\Delta\mu\,t$

➡ kinetic Wulff theorem $\dfrac{K(\boldsymbol{n})}{h(\boldsymbol{n})} = \dfrac{1}{\Delta\mu\,t} = c^{st}$

similar to the equilibrium Wulff theorem $\dfrac{\gamma(\boldsymbol{n})}{h(\boldsymbol{n})} = \dfrac{\Delta\mu}{2\Omega}$

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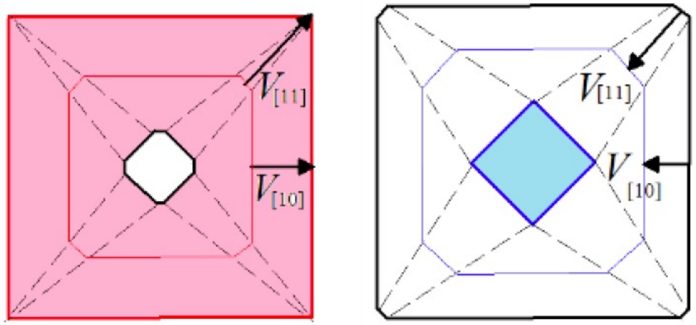
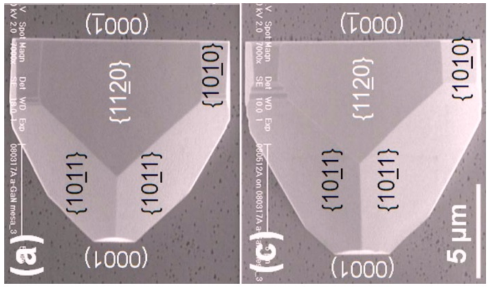
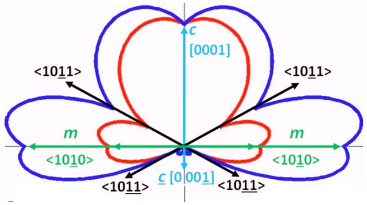


Ex: GaN

complex growth phenomena can be explained by kinetic Wulff plots





Sun 08

Crystals in and out of equilibrium

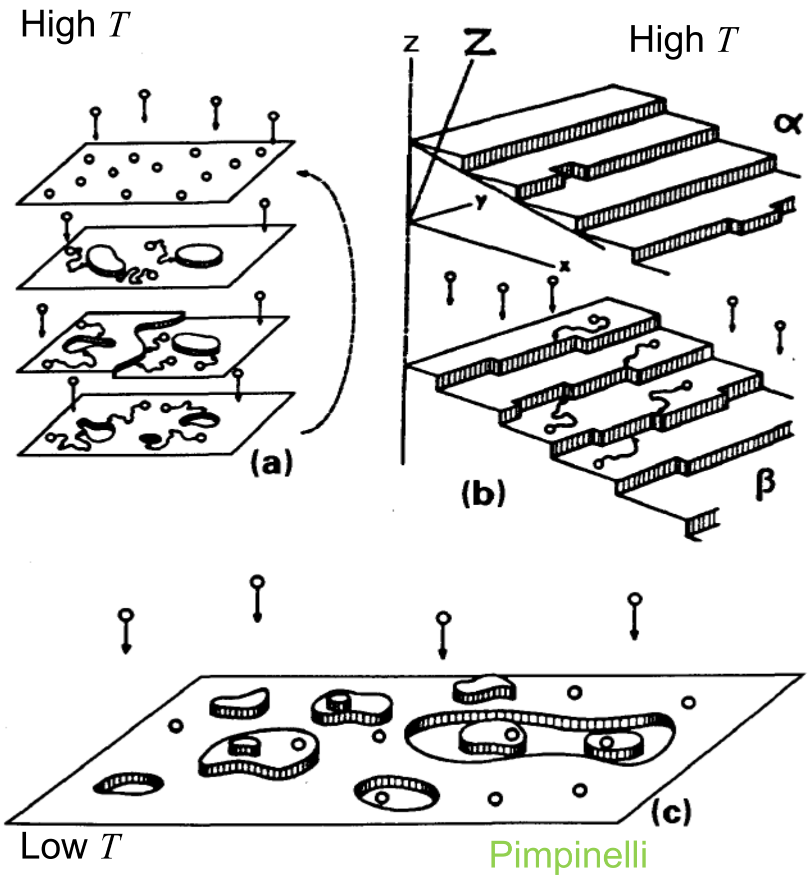
I. Crystal growth vs equilibrium

II. Equilibrium
    1. Phase transition
    2. Phase separation
    3. Equilibrium shape of crystals
        a. Gibbs-Curie-Wulff theorem
        b. Wulff construction
        c. Kaischew construction
        d. Wulff today
        e. Continuous shape
        f. Continuous Wulff construction
        g. Inverse Wulff construction
    4. Atomistic crystal shapes
    5. Step fluctuations on vicinal surfaces
    6. Roughening transition
        a. Jackson model
        b. Morphologies
        c. Mean-field approach
        d. Correlations
        e. Renormalisation group
        f. Experiments

III. Out-of-equilibrium properties
    1. Ideal laws
    2. Kinetic Wulf theorem
    3. Kinetics-limited growth
        a. Nucleation
        b. Step growth
        c. Noise induced roughening
        d. Growth under constraint
    4. Theoretical tools for epitaxy

3. Kinetics-limited growth

Beyond ideal laws, we need to understand the atomistic processes that govern growth



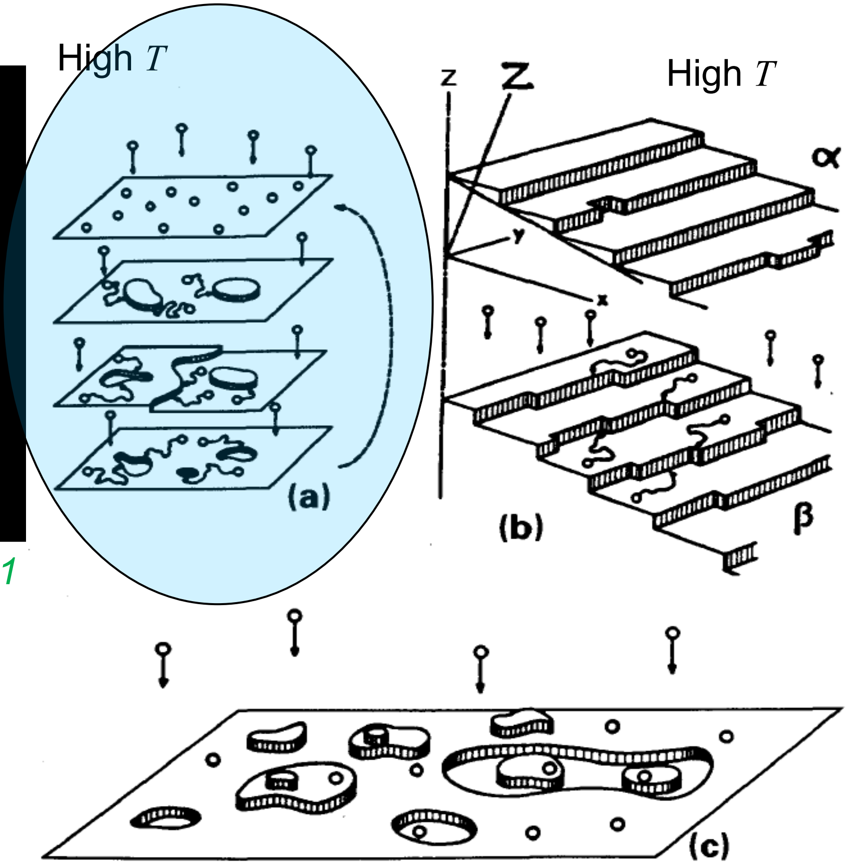
Pimpinelli

3. Kinetics-limited growth

Beyond ideal laws, we need to understand the atomistic processes that govern growth

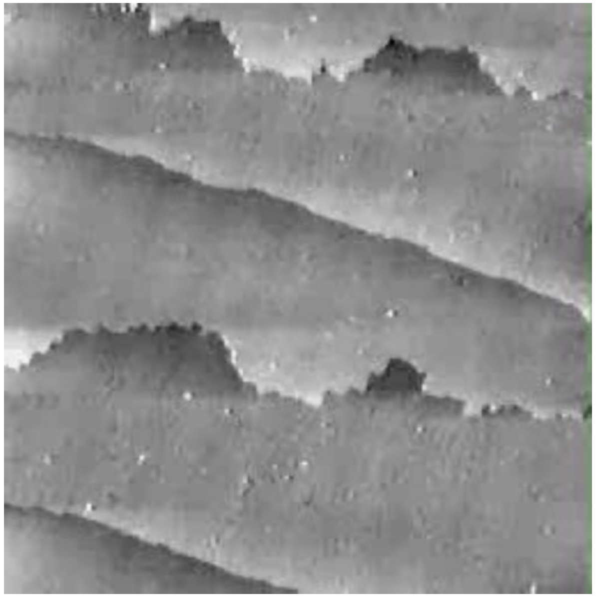
Nominal Si (111) $T=775\text{K}$

Vidéo 1



Pimpinelli

Vicinal Si (001) $T=725\text{K}$

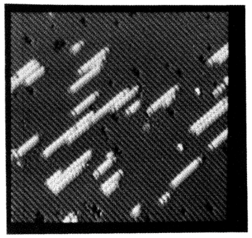


Voigtländer

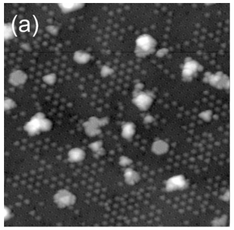
www.kfa-juelich.de/video/voigtlaender

Vidéo 2

Si/Si(001)



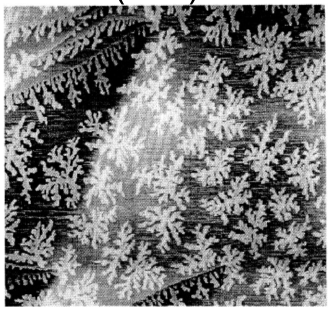
Ge/Ge(001)



Mo 91

Cherepanov 02

Au/Ru(001)



Hwang 91

Crystal growth by molecular beam epitaxy

Kinetic Monte Carlo simulation by Vladimir Kaganer
3D visualization by Roman Shayduk
Video and sound by Gerd Paris

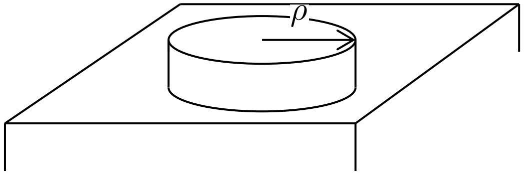
Paul-Drude-Institut für Festkörperelektronik, Berlin, Deutschland
www.pdi-berlin.de

https://www.youtube.com/watch?v=NsGRKSV8yH8

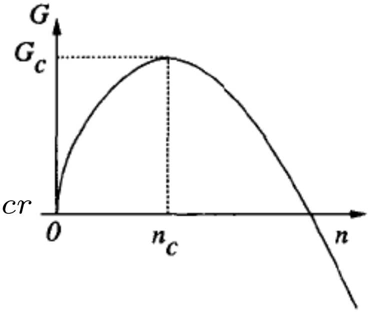
Vidéo 3

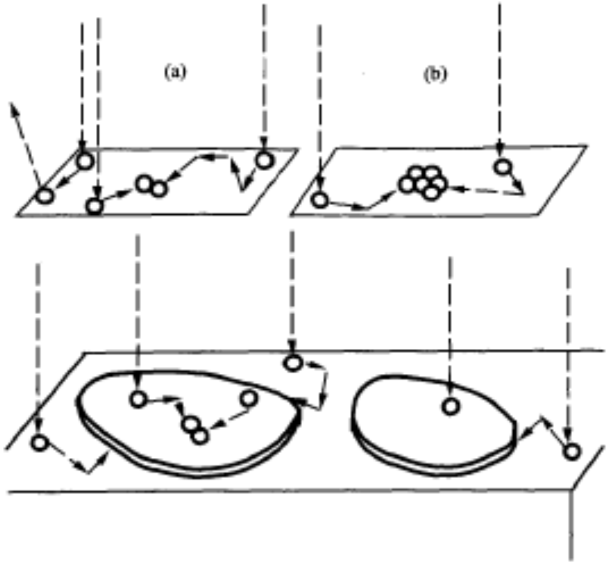
3.a Nucleation

Thermodynamic theory of nucleation

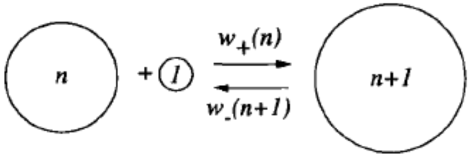


$G(n) = -\Delta\mu\, n + 2\pi^{1/2} a\, \delta \sqrt{n}$ with $\Delta\mu = \mu_{ad} - \mu_{cr}$





Rate theory of aggregation/desorption

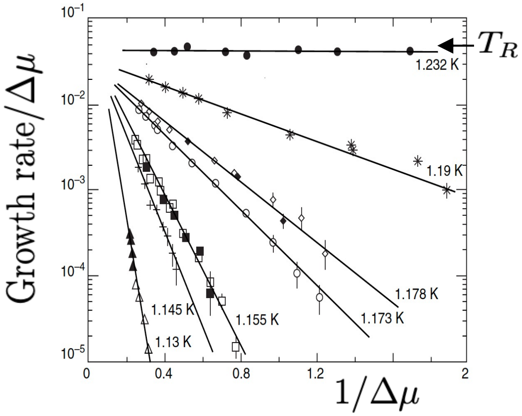


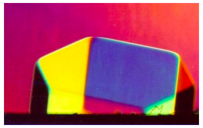
$$\frac{\partial c(n)}{\partial t} = w_+(n-1)c(n-1) - w_-(n)c(n) + w_-(n+1)c(n+1) - w_+(n)c(n)$$

… growth rate $v_z \propto e^{-G_c/k_BT}$

Below the roughening transition

$$v_z \sim \Delta\mu^{\,5/6} e^{-\beta \frac{\pi a^2 \delta^2}{3\Delta\mu}}$$





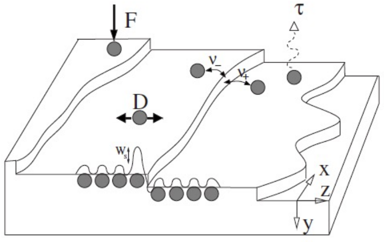
⇨ Cf Alberto Pimpinelli Monday 18h

3.b Step growth

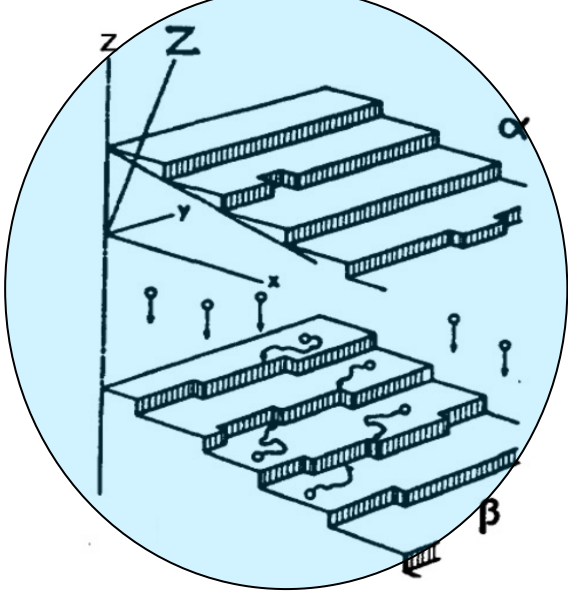
Coarse-grained approach with steps and diffusion equation on terraces

Burton-Cabrera-Frank model

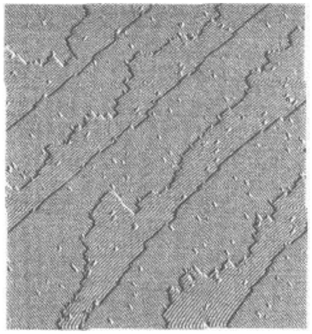
$$\frac{\partial c_n}{\partial t} = F - \frac{c_n}{\tau} + D_s \Delta c_n$$



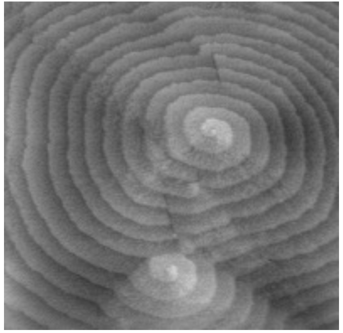
Misbah 10



Si (001)



α–amylase protein

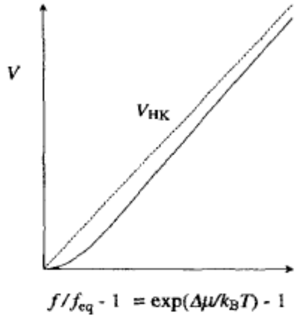


Lagally 90

spiral growth

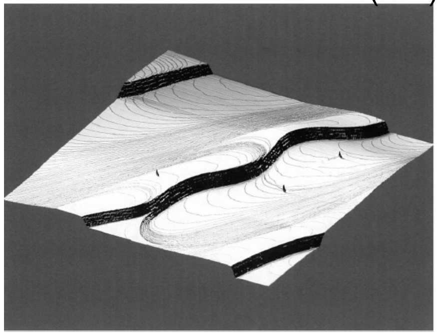
$$v_z \propto \xi^2 \tanh(\xi_0/\xi)$$

$$\xi = e^{\Delta\mu/k_BT} - 1$$

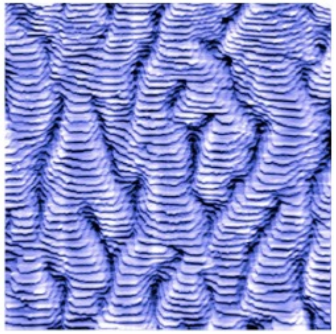


… step-bunching and step-meandering **instabilities**

Si (111)



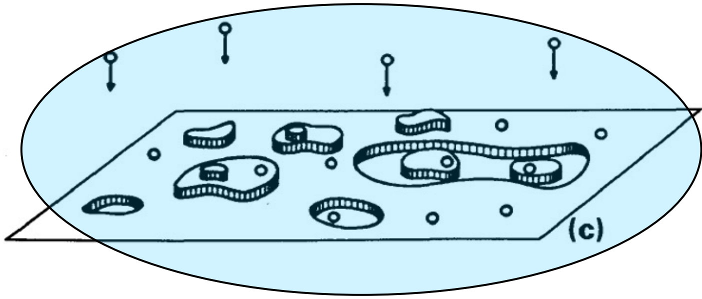
Cu(1 1 17)



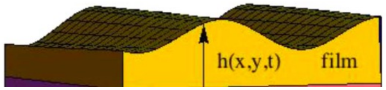
Jeong 99

Cf Alberto Pimpinelli
Wednesday 8h30

3.c Noise induced roughening



Coarse-grained approach with steps and



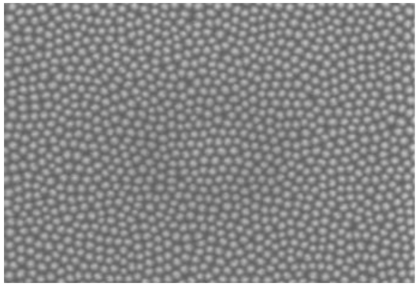
Mass evolution : $\dfrac{\partial h}{\partial t} = G[h; x, t] + \eta(x, t)$

Edwards-Wilkinson $\dfrac{\partial h}{\partial t} = F + \nu \Delta h + \eta(x, t)$

Kardar-Parisi-Zhang $\dfrac{\partial h}{\partial t} = \nu \Delta h + \dfrac{\Lambda}{2} \boldsymbol{\nabla} h^2 + \eta(x, t)$

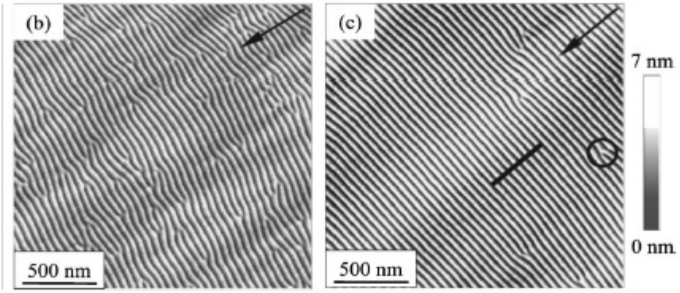
… self-similar solutions and dynamical exponents

GaSb (100)



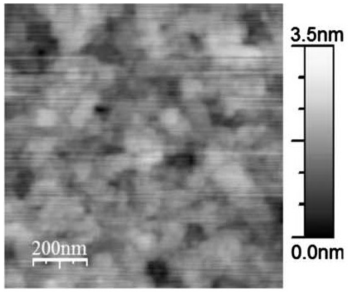
Facsko 99

Kr+/Si

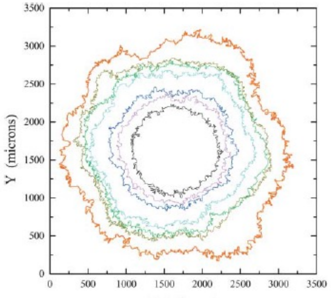


Ziberi 05

Ar+/Si(100)

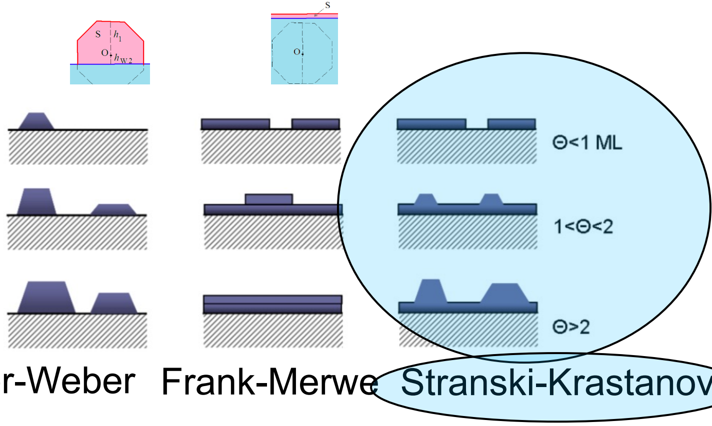


Ozaydin 08



Bru 03

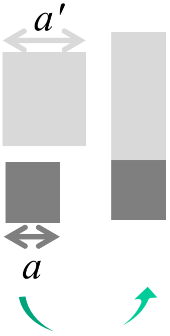
3.d Growth under constraint

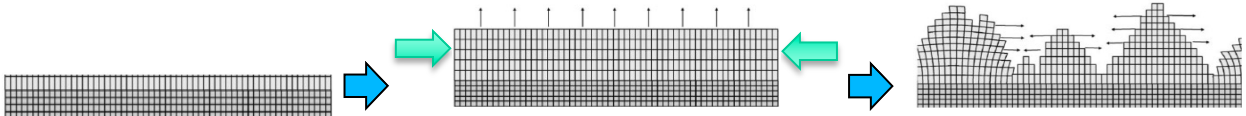


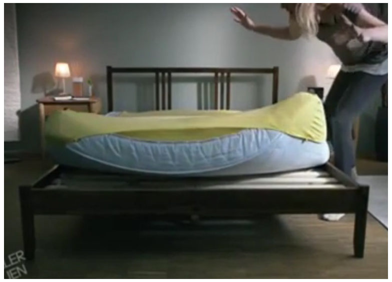
In crystals, new growth mode % liquid when strain occurs due to the film/substrate lattice mismatch

Partial/complete wetting explains growth modes similar to liquids

Strain explains an hybrid mode specific to solids





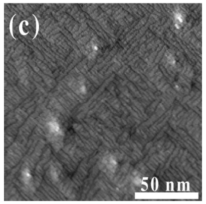


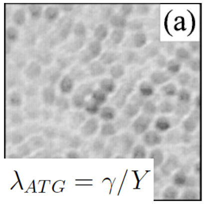
Morphological evolution
(i) surface diffusion
(i) without dislocation

It may be rationalized either by strain-induced nucleation (high strain)

or by the Asaro-Tiller-Grinfel'd instability (low strain)

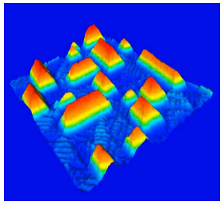
Vailonis 00
Ge on Si





$\lambda_{ATG} = \gamma / Y$

$Si_{0.6}Ge_{0.4}$ on Si
Sutter 00

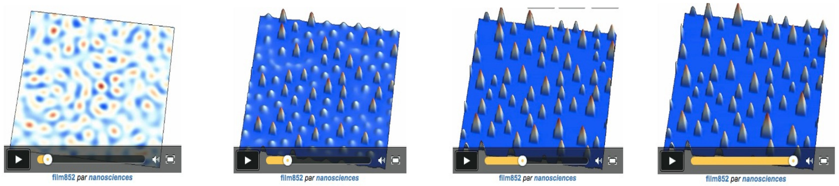


Voigtlander

Non-linear analysis of the instability

$$\frac{\partial h}{\partial t} = \Delta \Big\{ -\gamma(h)\Delta h + \gamma'(h) - \mathcal{H}_{ii}(h) + 2h\Delta h + \nabla h^2 + 2\mathcal{H}_{ij}\left[h\mathcal{H}_{ij}(h)\right] + \mathcal{H}_{ij}(h)\mathcal{H}_{ij}(h) \Big\}$$

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



Aqua 13 *Vidéo 4-5*

Cf Pierre Müller
Tuesday 14h

Crystals in and out of equilibrium

I. Crystal growth vs equilibrium

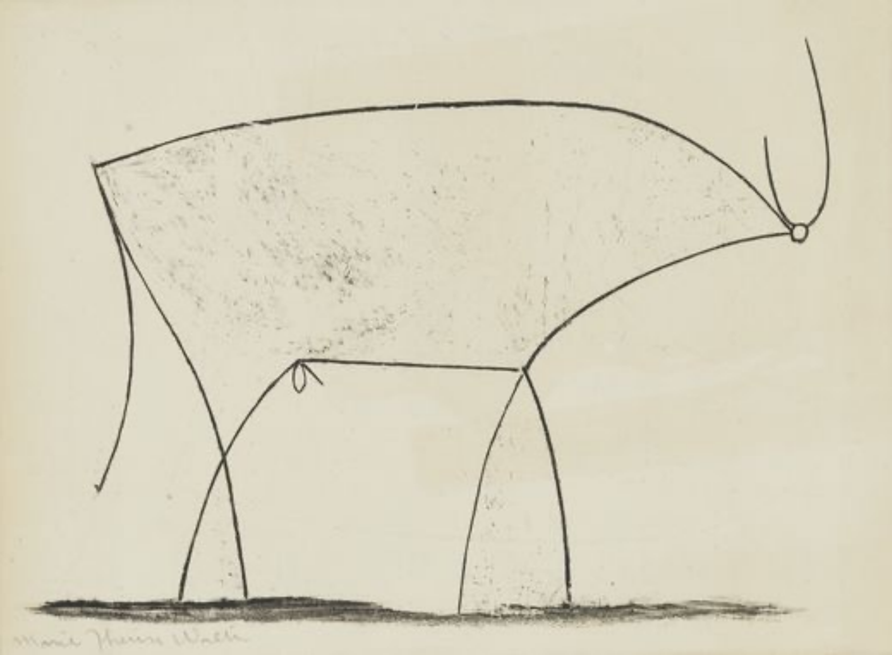
II. Equilibrium
  1. Phase transition
  2. Phase separation
  3. Equilibrium shape of crystals
    a. Gibbs-Curie-Wulff theorem
    b. Wulff construction
    c. Kaischew construction
    d. Wulff today
    e. Continuous shape
    f. Continuous Wulff construction
    g. Inverse Wulff construction
  4. Atomistic crystal shapes
  5. Step fluctuations on vicinal surfaces
  6. Roughening transition
    a. Jackson model
    b. Morphologies
    c. Mean-field approach
    d. Correlations
    e. Renormalisation group
    f. Experiments

III. Out-of-equilibrium properties
  1. Ideal laws
  2. Kinetic Wulf theorem
  3. Kinetics-limited growth
    a. Nucleation
    b. Step growth
    c. Noise induced roughening
    d. Growth under constraint
  4. Theoretical tools for epitaxy

4. Theoretical tools useful for epitaxy

Need for dynamical modelization

What do you see ?



Picasso

A line that makes you **think** of a bull :
- simple enough
- realistic enough

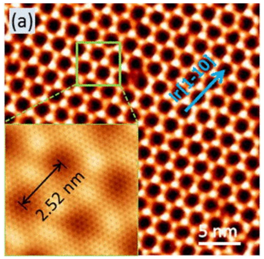
...but **not** a bull

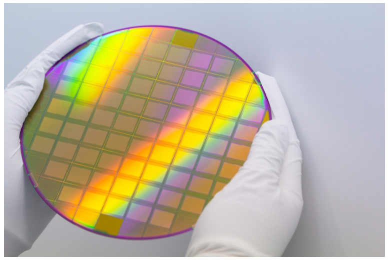
Modelization :
- skips irrelevant details to derive a simple enough model
- includes enough features to get a realistic description

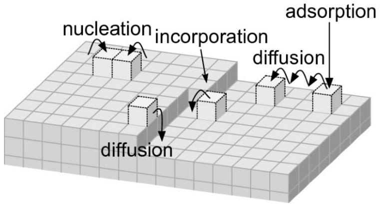
4. Theoretical tools for epitaxy

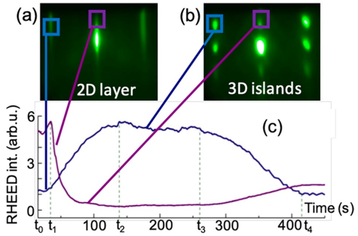
Need a description that do the splits

- From nm to μm ... **cm**
- from picoseconds to **hours**

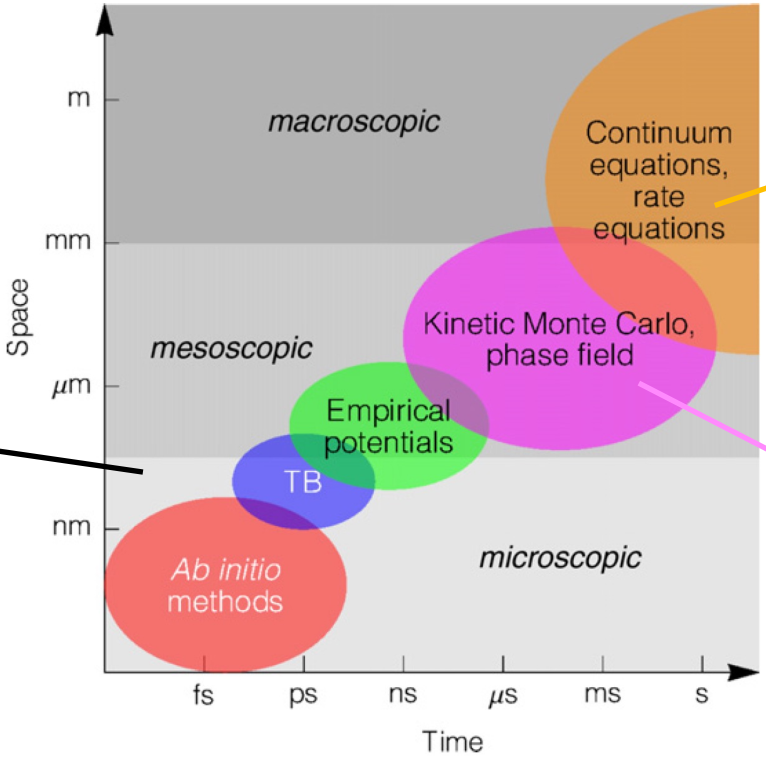


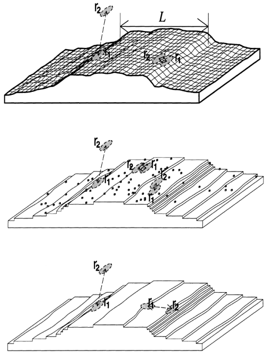


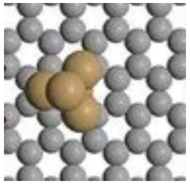


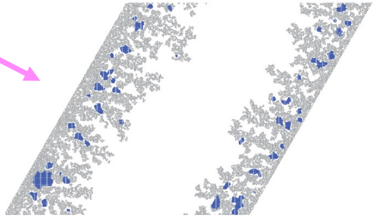


➡ multi-scale analysis

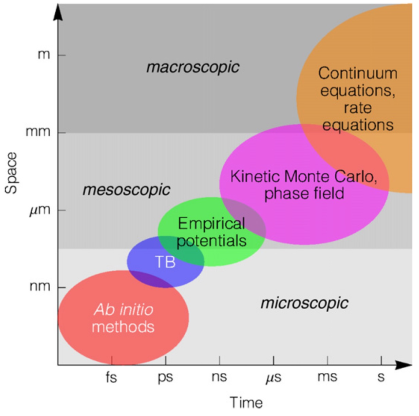








4. Theoretical tools for epitaxy



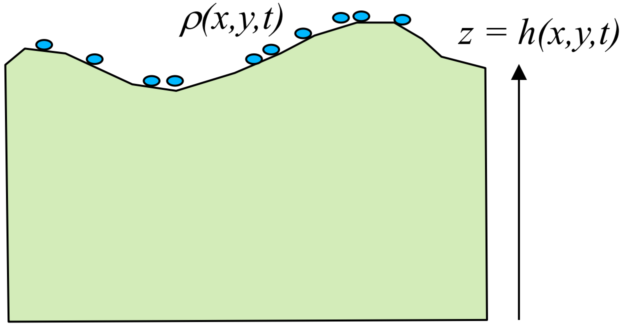
✓ Continuum equations

enable to describe

- macroscopic length scales
- macroscopic time scales
- a dynamical framework

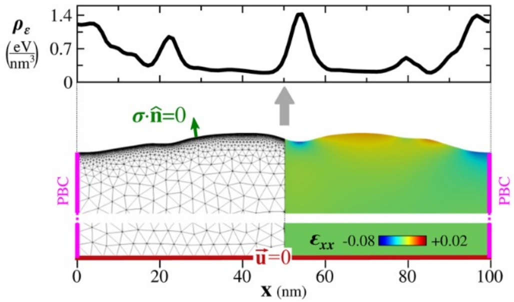
$$\frac{\partial h}{\partial t} = \mathcal{F}\left[h, \frac{\partial h}{\partial x}\ldots\right]$$

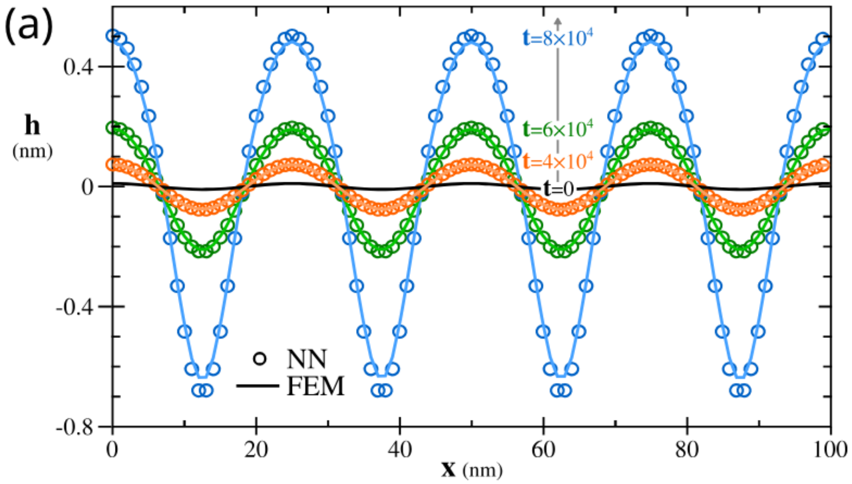
$$\frac{\partial \rho}{\partial t} = \mathcal{F}\left[c, \frac{\partial c}{\partial x}, h\ldots\right]$$



Ex.: Can be implemented with deep-learning methods to integrate costly finite element methods integration

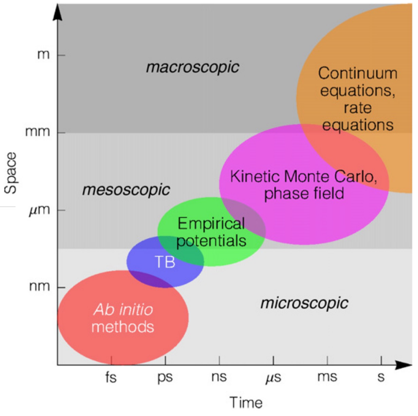
$$\frac{\partial h}{\partial t} = M\sqrt{1+h'^2}\,\frac{\partial^2 \mu}{\partial s^2} + f,$$





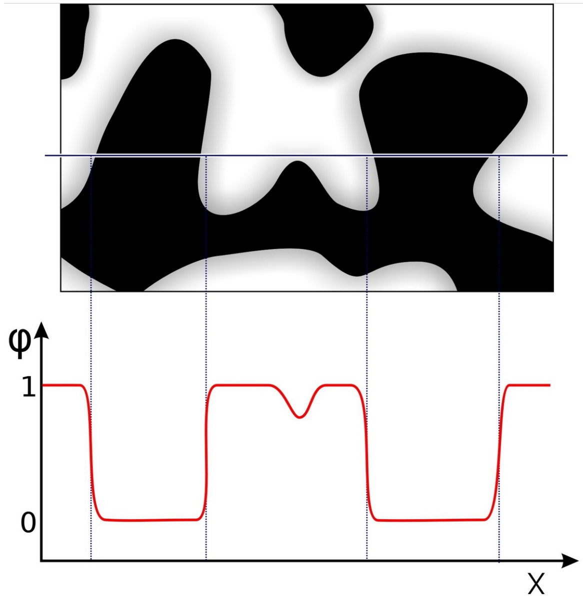
Lanzoni 24

4. Theoretical tools for epitaxy



- ✓ Continuum equations
- ✓ **Phase-field methods**

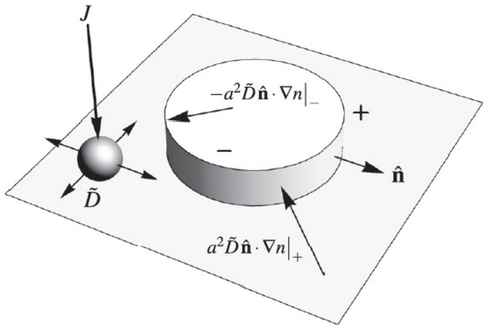
Replace a sharp interface problem by
a continuous field with fast local variations
and a free energy

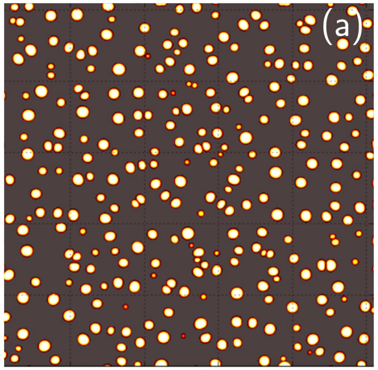


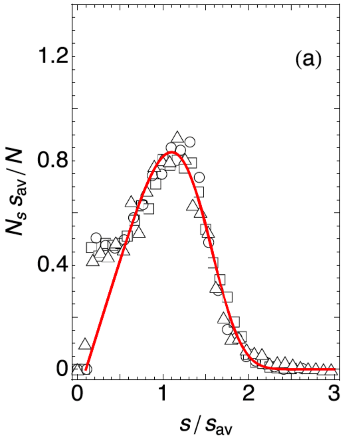
$$F[e,\varphi] = \int d\mathbf{r}\left[K|\nabla\varphi|^2 + h_0 f(\varphi) + e_0 u(\varphi)^2\right]$$

Ex.: Used to investigate epitaxial kinetics and the sub-monolayer aggregation

$$\frac{\partial n}{\partial t} = a^2\tilde{D}\nabla^2 n + \tilde{J},$$

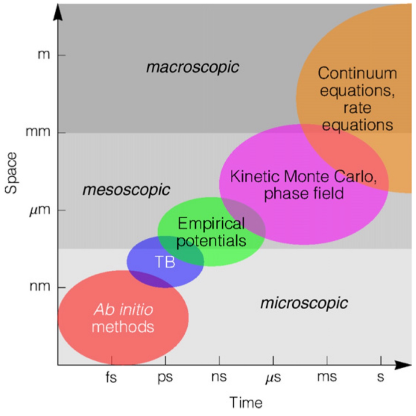






De Boer 18

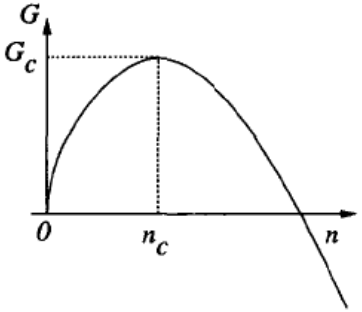
4. Theoretical tools useful epitaxy

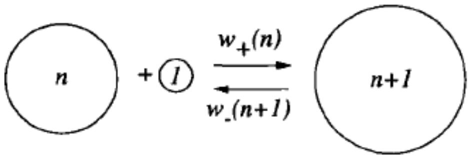


- ✓ Continuum equations
- ✓ Phase-field methods
- ✓ **Nucleation theory**

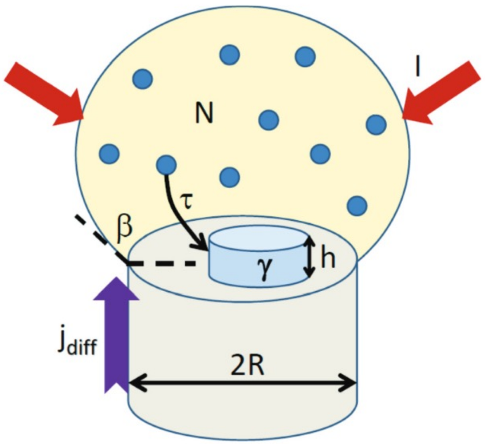
kinetics of crossing an energy barrier,
out-of-equilibrium statistical physics

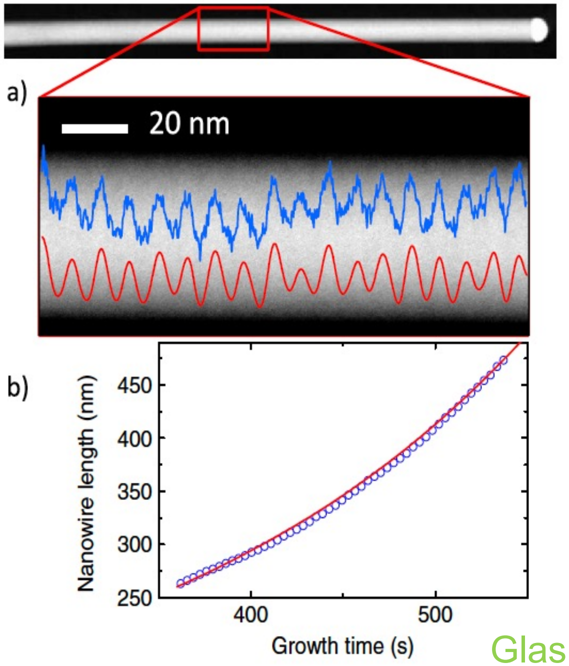
$$J \propto Z w_{+}(n_c) c_{\infty} \exp(-G_c/k_B T)$$





Ex.: InPAs growth via Vapor-Liquid-Solid growth and nucleation anti-bunching

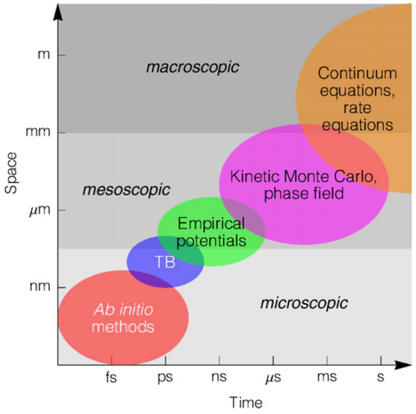




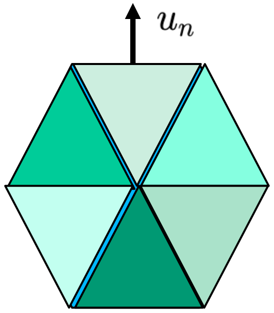
Glas 10

Cf Frank Glas
Tuesday 16h

4. Theoretical tools useful epitaxy



- ✓ Continuum equations
- ✓ Phase-field methods
- ✓ Nucleation theory
- ✓ **Local thermodynamics**
  - mass conservation $u_n = -\Omega\nabla_s\cdot\mathbf{J}_s + f_n$
  - linear response (Onsager) $\mathbf{J}_s = -M\nabla_s\mu$ *vs* $K\Delta\mu$
  - appropriate free energy … μ

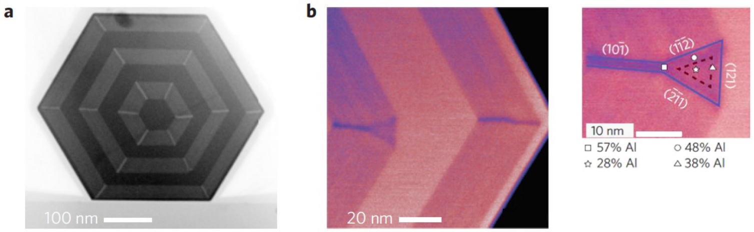


Ex: GaAs/AlGaAs nanowires with quantum dots

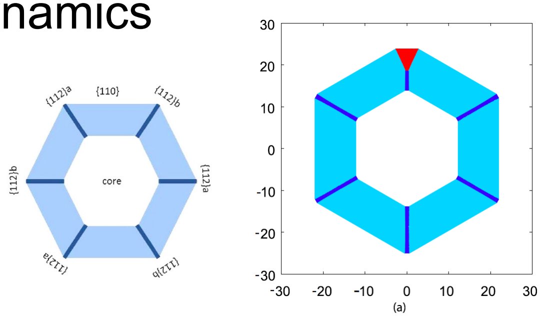
the growth shapes can lead to complex structures

… that can be reproduced by a generalization

of the kinetic Wulff shapes with a facet thermodynamics

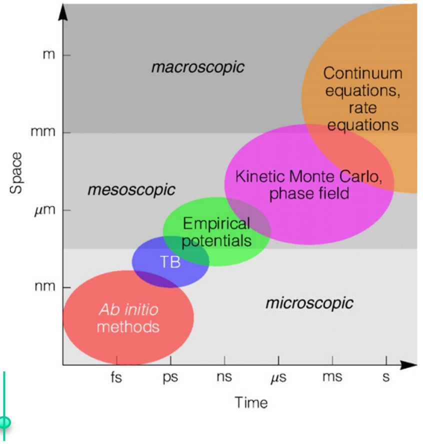


Heiss 13

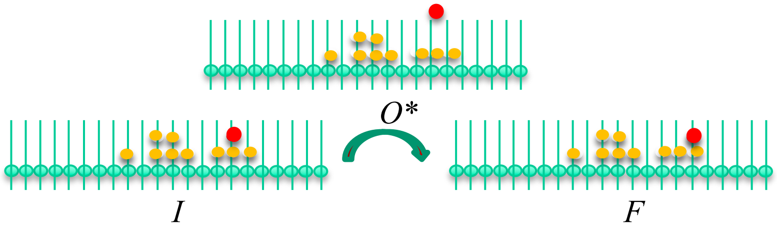


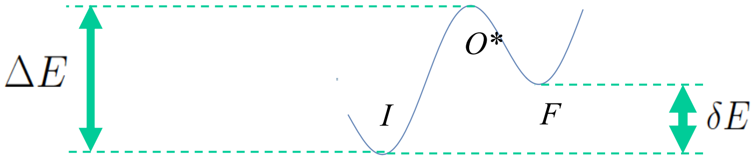
Zhang 16

4. Theoretical tools for epitaxy



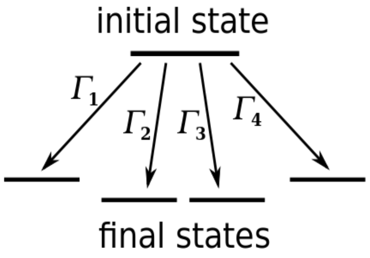
- ✓ Continuum equations
- ✓ Phase-field methods
- ✓ Nucleation theory
- ✓ Local thermodynamics
- ✓ **Kinetic Monte-Carlo**

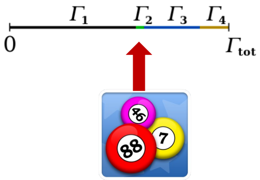




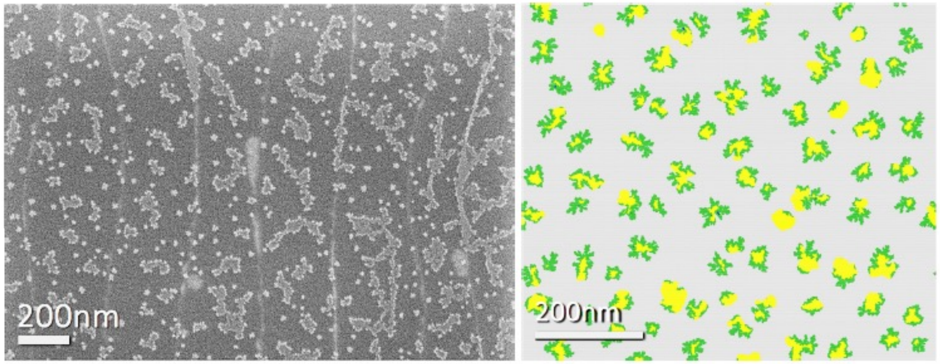
Dynamical events described as a Markov chain
& transition rates related to energy barriers

$$\Gamma \propto \exp\left[-\Delta E/k_B T\right]$$



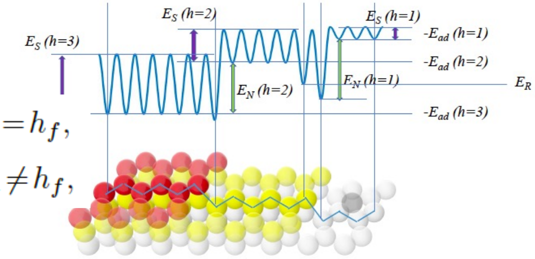


Ex: Growth of silicene on graphene



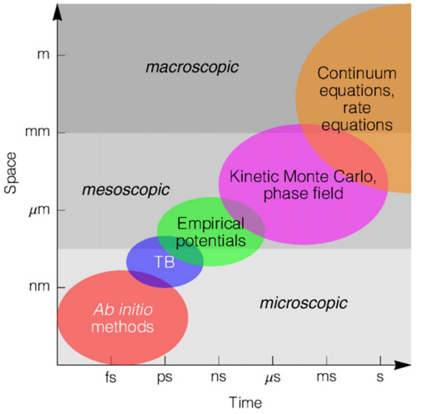
Thermodynamics accounting for adsorption energy,
wetting and edge effects

$$\begin{aligned}\Delta E &= E_S(h_i) + n_i E_N(h_i) & \text{if } h_i = h_f,\\ &= -E_{ES}^{h_i/h_f} + E_{ad}(h_i) + n_i E_N(h_i) & \text{if } h_i \neq h_f,\end{aligned}$$

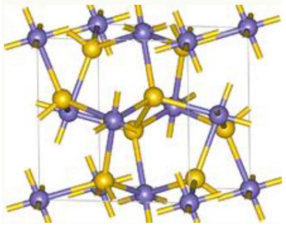


Cf Kejian Wang
poster Tuesday 20h30

4. Theoretical tools for epitaxy



- ✓ Continuum equations
- ✓ Phase-field methods
- ✓ Nucleation theory
- ✓ Local thermodynamics
- ✓ Kinetic Monte-Carlo
- ✓ **Ab-initio molecular dynamics**

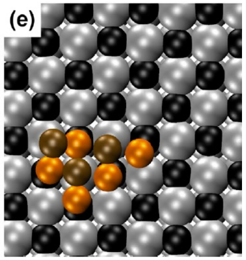


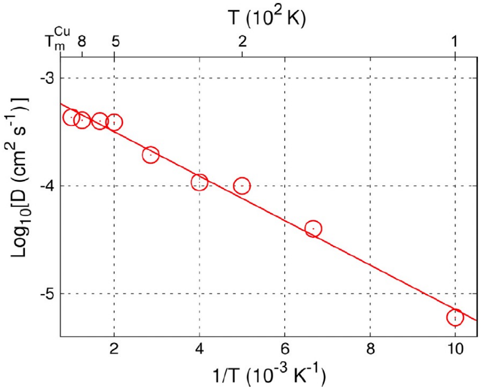
Solve Schrödinger equation with
controlled approximations
for the electronic part
(with/without deep learning)

$$\hat{H} = \hat{T}_n(\{\mathbf{R}\}) + \hat{T}_e(\{\mathbf{R}\}) + \hat{V}_{nn}(\{\mathbf{R}\}) + \hat{V}_{ne}(\{\mathbf{R}\},\{\mathbf{R}\}) + \underline{\hat{V}_{ee}(\{\mathbf{r}\})}$$

… then solve the classical dynamical equation for the ions $m\,\mathbf{a}_n = \sum \mathbf{F}_n$

Ex: diffusion coefficient and nucleation of Cu on TiN(001)

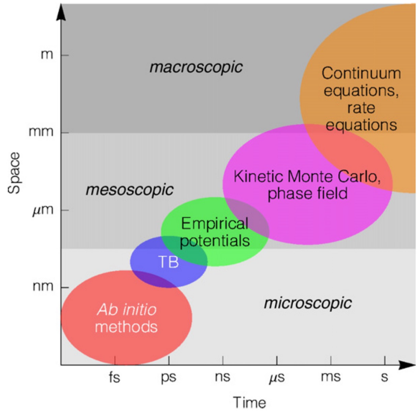




Sangiovanni 18

⇨ Cf Michele Amato Tuesday 8h

4. Theoretical tools for epitaxy



✓ Continuum equations

✓ Phase-field methods

✓ Nucleation theory

✓ Local thermodynamics

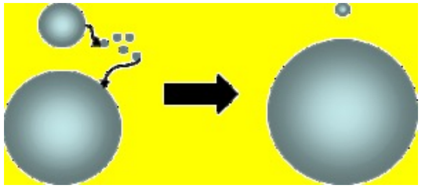
✓ Kinetic Monte-Carlo

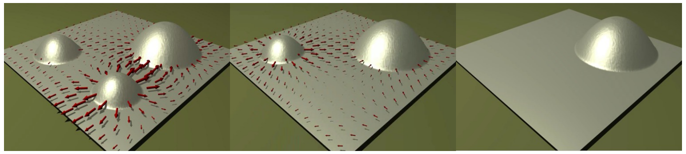
✓ Ab-initio molecular dynamics

✓ …

Other topics

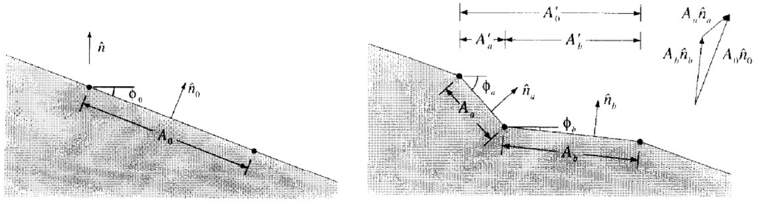
- Coarsening

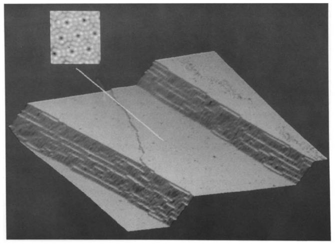




$$\langle N(t)\rangle \sim t^{\zeta}\,, \qquad \zeta = \frac{d}{3+d-D}$$

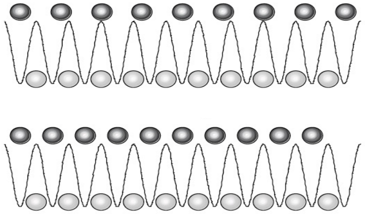
- Faceting transition



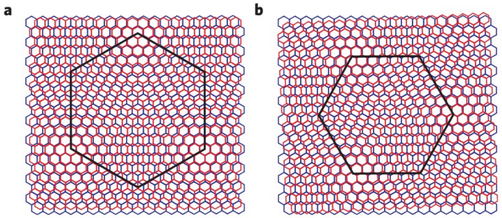


Williams 94

- Commensurate/inconmensurate

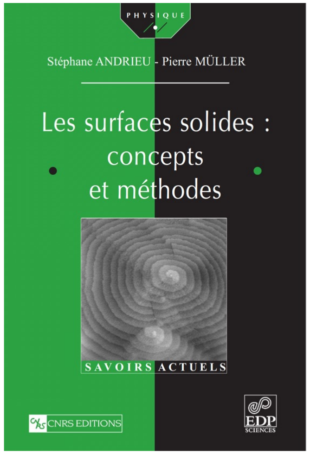


Gr on hBN



Woods 14

- …



PHYSIQUE

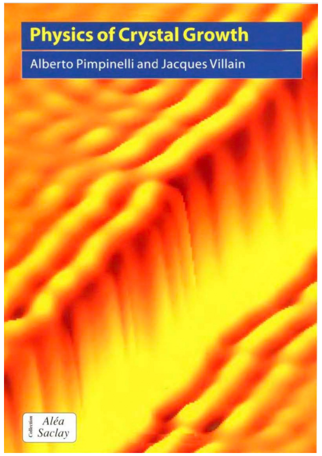
Stéphane ANDRIEU - Pierre MÜLLER

Les surfaces solides : concepts et méthodes

SAVOIRS ACTUELS

CNRS EDITIONS

EDP SCIENCES



Physics of Crystal Growth

Alberto Pimpinelli and Jacques Villain

Collection Aléa Saclay

⇨ cf

Stéphane Andrieu

Pierre Müller

Alberto Pimpinelli