



*Polytypic growth spirals on
a grain boundary*
(n-C₂₈H₅₈)

Two different habits of gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) crystal



5,5 cm - Zaragoza Aragón, Spain

[001] prismatic habit



14 cm - Naica Mine
Chihuahua, Mexico

platy -{010}

Gypsum, **green** by copper – 4 cm xls, Legnica, Lower Slesia, Poland

Acicular habit, **high nucleation frequency** (number of crystals $\text{cm}^{-3} \text{s}^{-1}$)

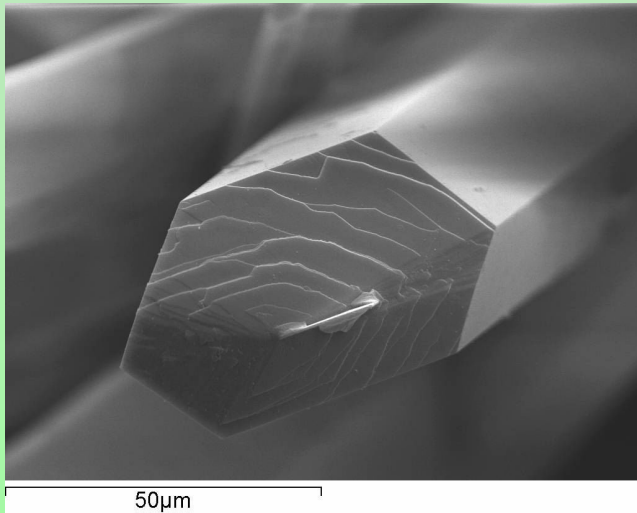


Why one observes in this case a so high nucleation frequency ?

*Why the gypsum crystals grown in the caves of Naica mine are very few in number (**very low nucleation frequency**) and very big (in size) ?*

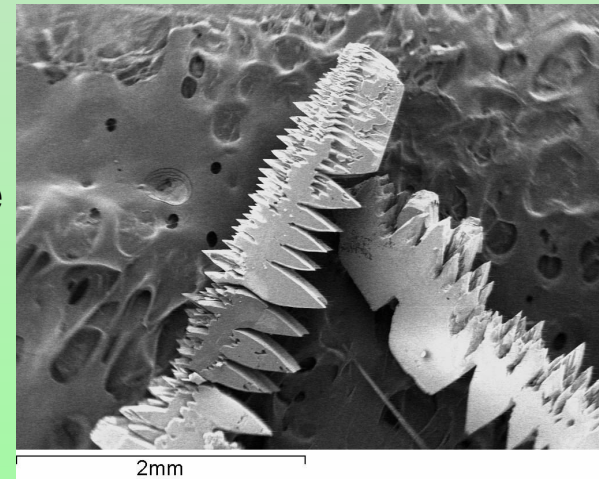
(J.M. Garcia Ruiz et al. 2007)





Copolymer
SR3

DTPMP
phosphonate



Why the **growth shapes** of gypsum crystals vary so much according to the growth parameters?

e.g. **adsorption / absorption of impurities** (the role of the solvent...)

Logical path:

first of all, the basic language

- equilibrium (+ adsorption)**
- kinetics mechanisms face by face (+adsorption)**
- growth habit**

*Some basic instruments
of the
Crystal Growth language*

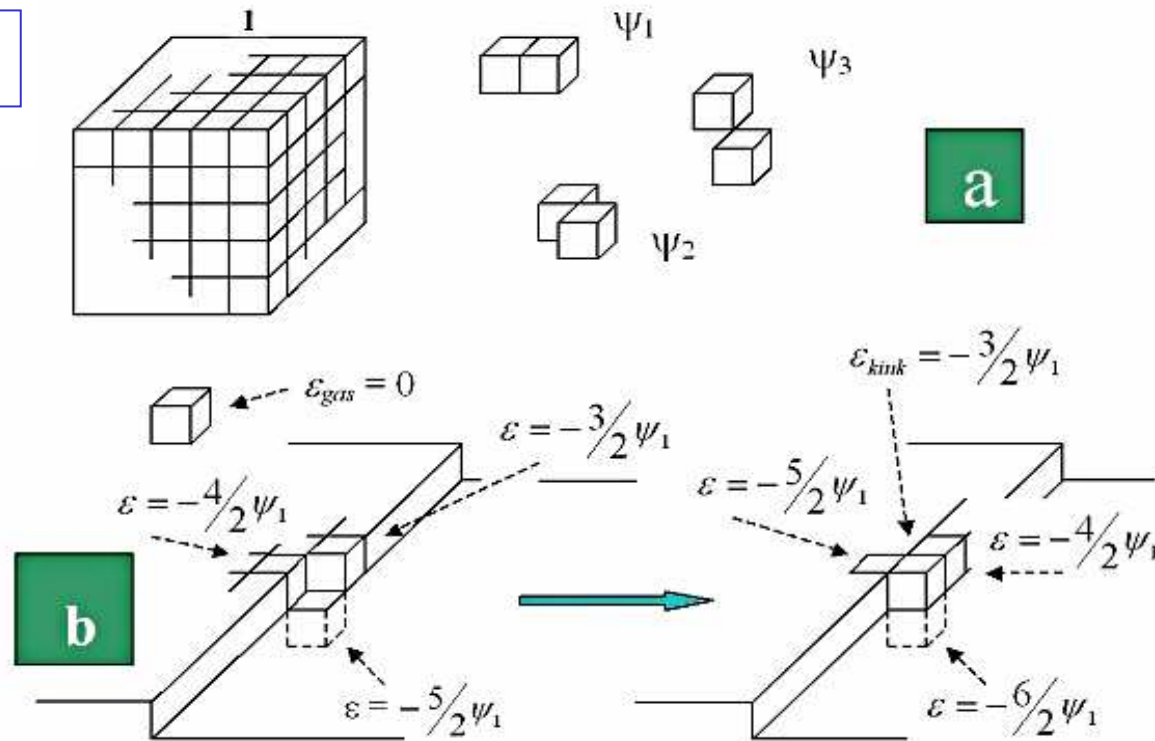
A **simple crystal** is needed for **modelling** both equilibrium and kinetics of crystals

The **KOSSEL's crystal** homopolar, simple cubic

Separation work between :

	1 st	2 nd	3 rd	nearest neighbours
→	ψ_1	ψ_2	ψ_3	

$$\psi_1 > \psi_2 > \psi_3$$



- ♣ When an atom enters a kink, there is a **transition in the potential energy**, the difference between final and initial stage being: $-3\psi_1$ (*1st neighbours*)

potential energy in the **vapour** $\varepsilon = 0$

↓

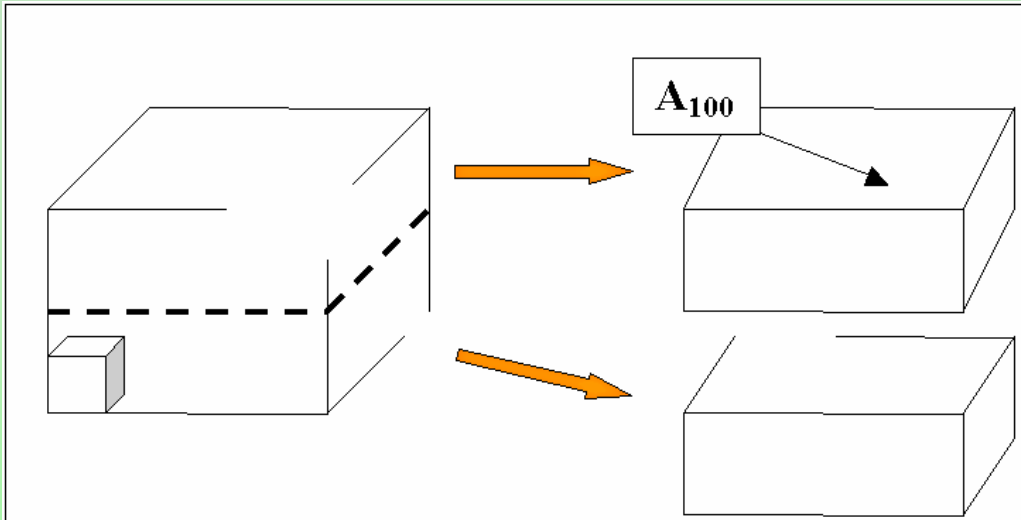
in the **kink** $\varepsilon = -3\psi_1$

- ♣ This is equivalent to say that the **separation work for an atom in a kink** is (*1st neighbours*)

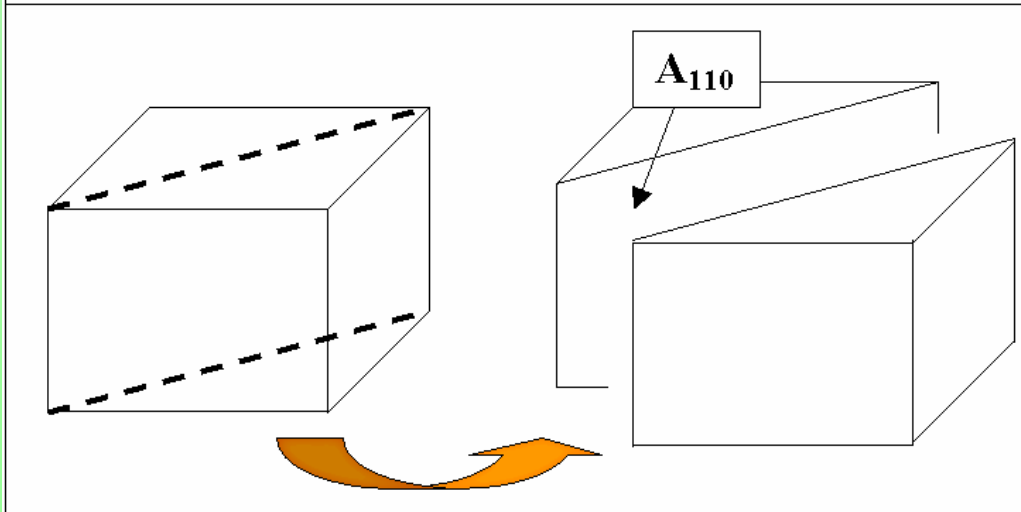
$$\phi_{\text{kink}} = 3\psi_1$$

specific surface energy of a $\{hkl\}$ form $\rightarrow \gamma_{hkl}$

.... within the Born-Stern approximation \rightarrow Kossel's crystal (*first neighbours*)



$$\gamma_{100} = \frac{W_{sep}^{100}}{2A_{100}} = \frac{n^2 \varphi}{2n^2 a^2} = \frac{\varphi}{2a^2}$$



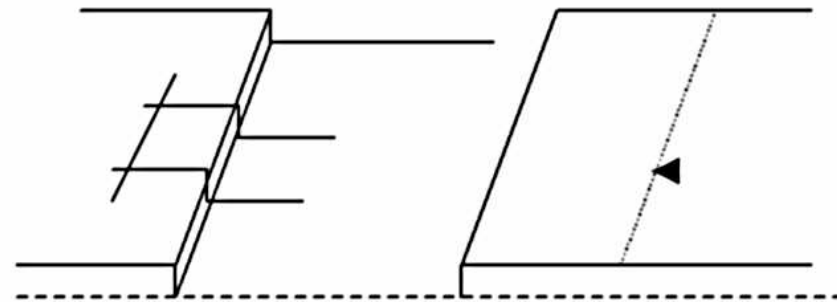
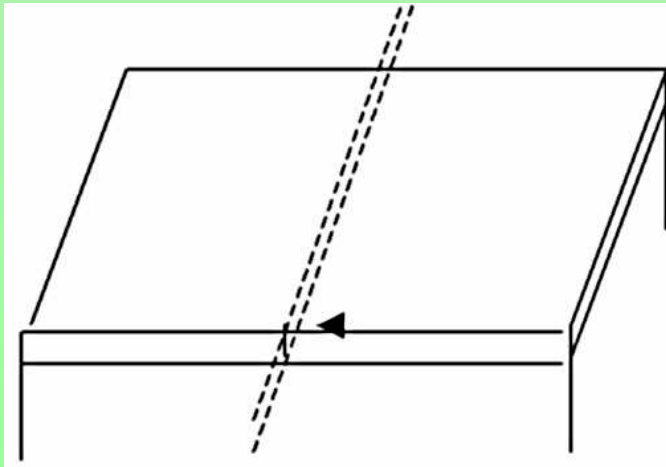
$$\gamma_{110} = \frac{W_{sep}^{110}}{2A_{110}} = \frac{2n(n-1)\varphi}{2[n(n-1)a \times a\sqrt{2}]} = \frac{\varphi}{\sqrt{2}a^2}$$

then:
 $\gamma_{110} > \gamma_{100}$
 the simplest way to demonstrate the anisotropy of the specific surface energy of crystals

specific edge energy

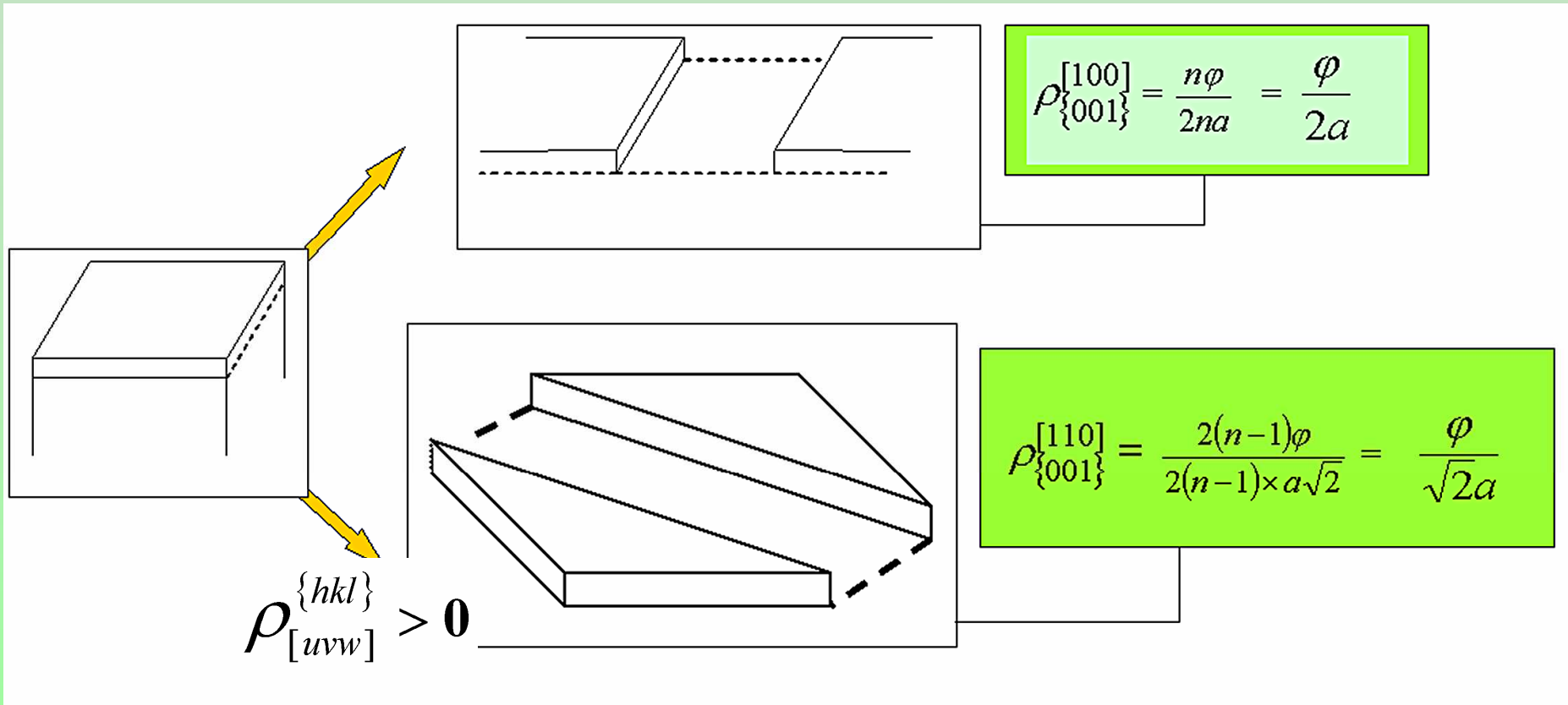
$$\rho_{[uvw]}^{\{hkl\}} = \frac{W_{\text{separation}}^{[uvw]}}{2l_{[uvw]}}$$

the work to be spent in order to
generate a unit length of **a new step** [uvw]
 on a given {hkl} face



The calculation is made in analogy with the Born-Stern definition

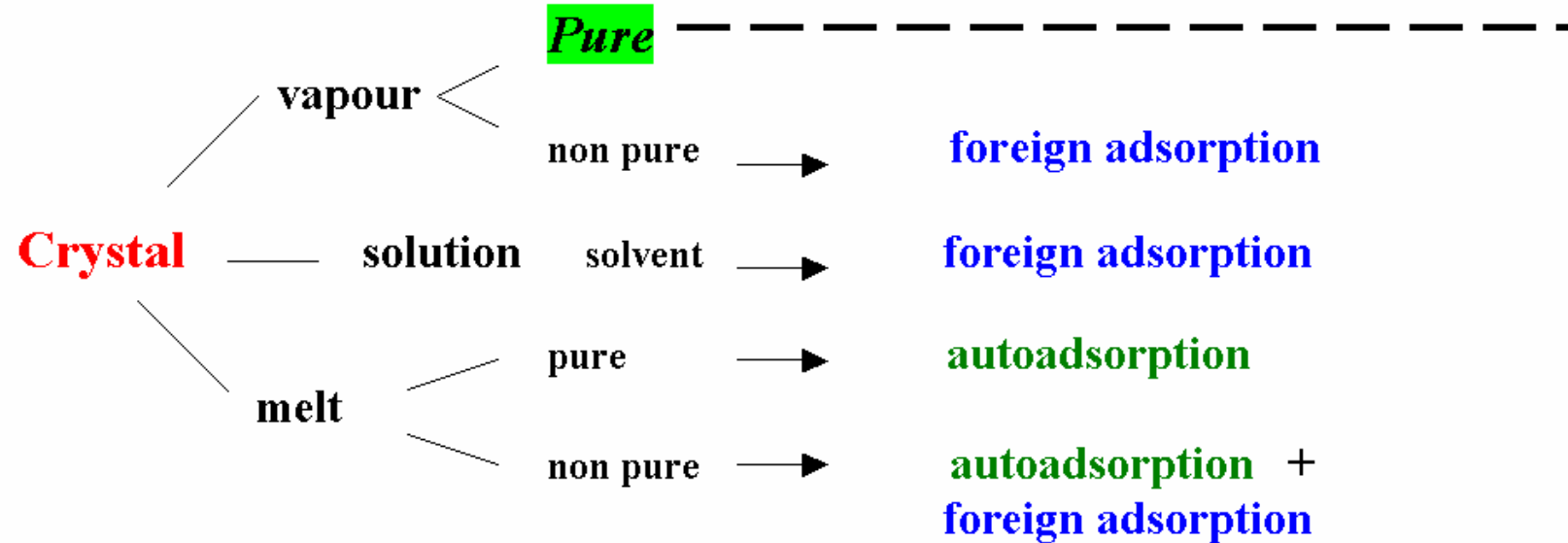
...once again the most simple example : the **Kossel's crystal**



• also the *specific edge energy* reflects the *anisotropy of a crystal surface*

• $\rho_{[uvw]}^{\{hkl\}} > 0$ represents the condition for $[uvw]$ *edge - step stability*

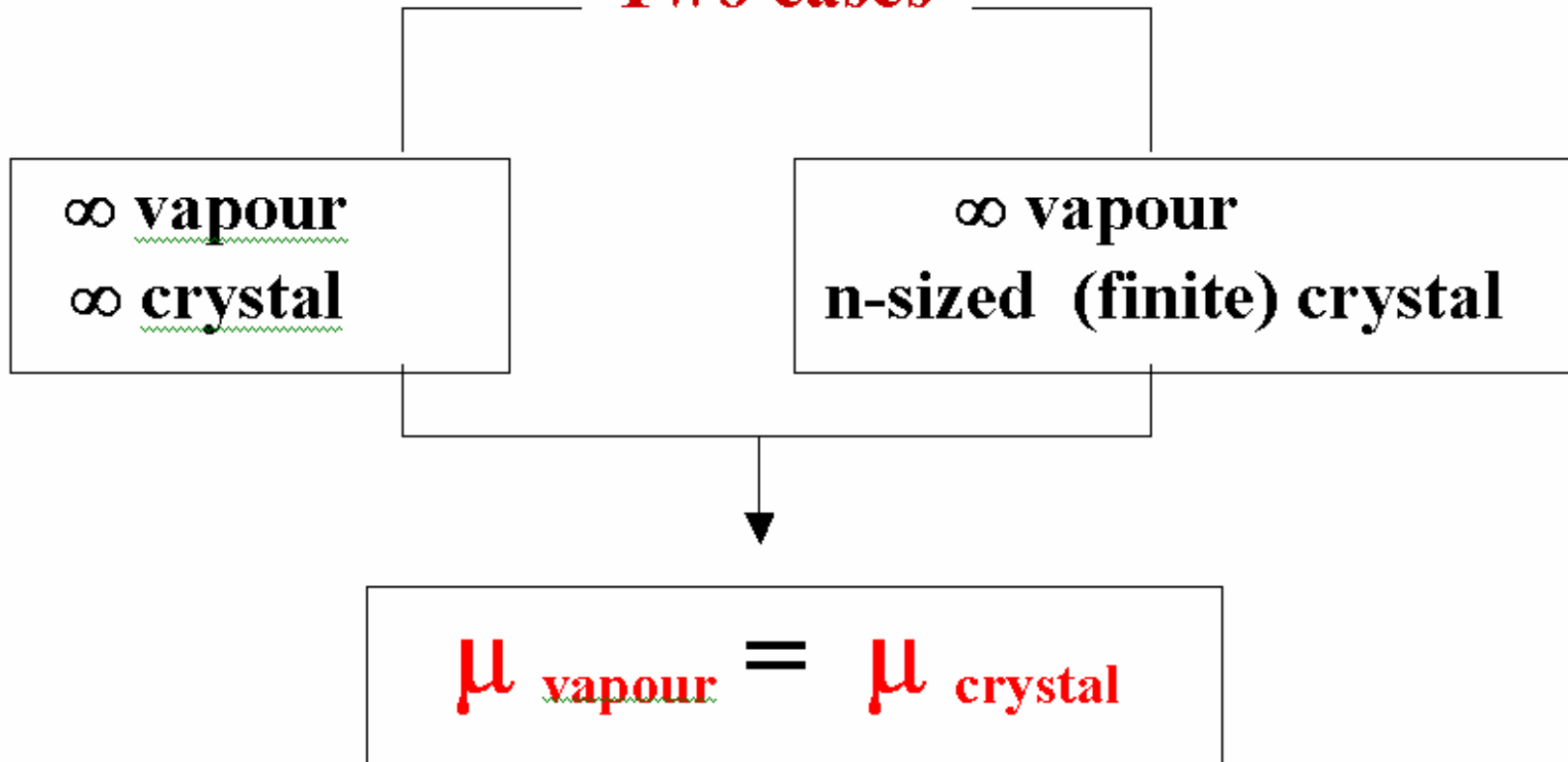
Equilibrium crystal – mother phase



The system can be described **exactly** through the statistical thermodynamics **only** for **monoatomic ideal crystal** and **monoatomic ideal vapour**

two cases

Two cases



Equilibrium

∞ vapour \rightleftharpoons ∞ crystal

$$\mu_v = \varepsilon_v - kT \ln \frac{p_\infty}{(2\pi m)^{3/2} (kT)^{5/2} h^{-3}}$$

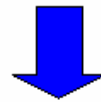
$$\mu_{c,\infty} = \varepsilon_{c,\infty} - kT \ln [(kT)^3 (h\nu)^{-3}]$$

$\mu_v = \mu_{c,\infty}$ at equilibrium

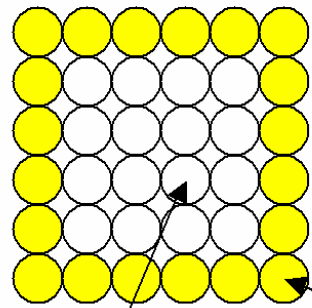
$$p_\infty = (2\pi m)^{3/2} (kT)^{-1/2} \nu^3 \exp \left[- (\varepsilon_v - \varepsilon_{c,\infty}) / kT \right]$$

where $(\varepsilon_v - \varepsilon_{c,\infty}) = \varphi_{c,\infty}$

represents the mean evaporation work
of the infinite crystal



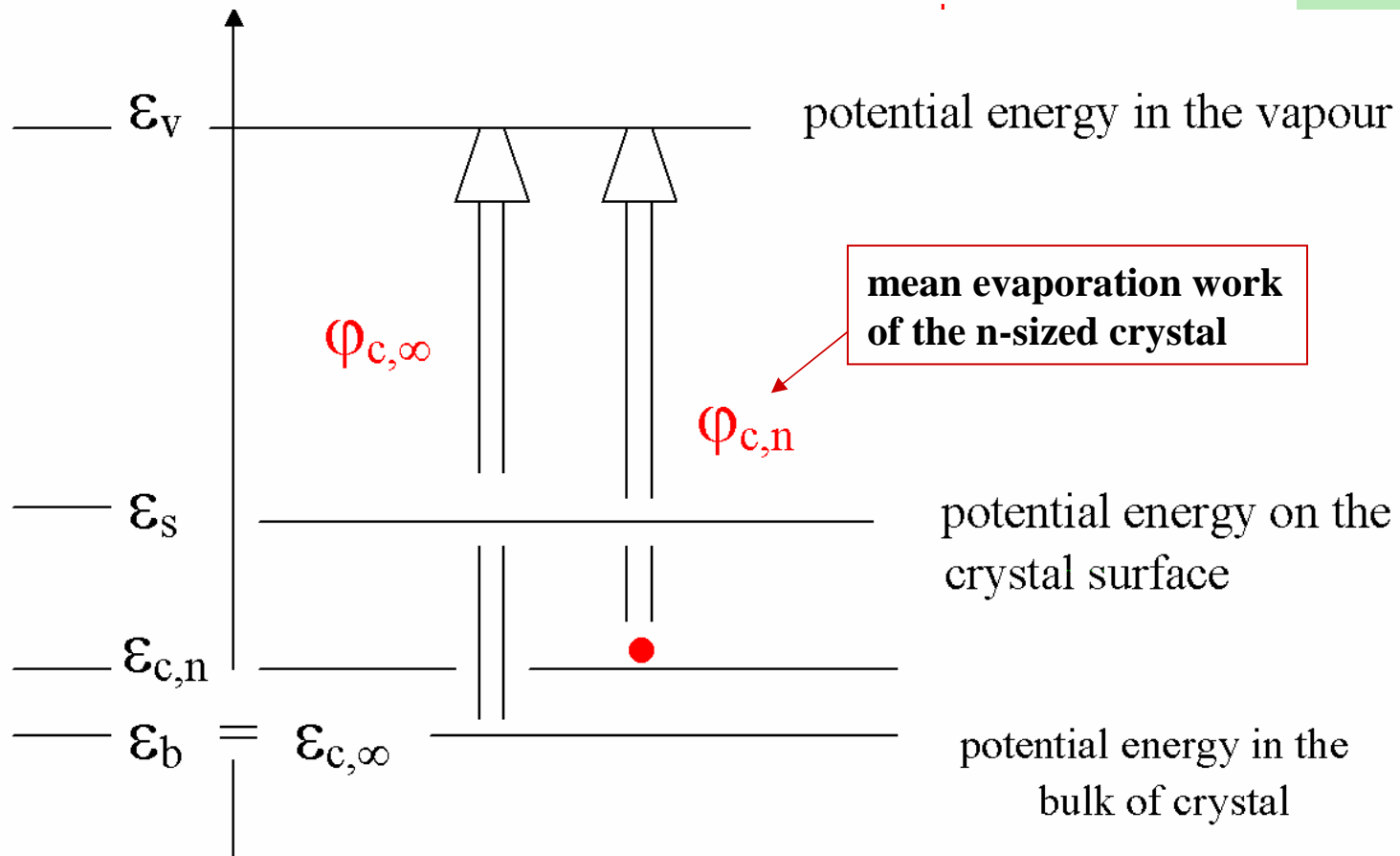
the equilibrium of an ∞ crystal only depends
on the pressure p_∞ of its own vapour



Equilibrium

n - sized crystal \leftrightarrow ∞ vapour

n_s number of atoms on the surface



$\varphi_{c,n} = (\varepsilon_v - \varepsilon_{c,n})$ is the mean evaporation work of the
n-sized crystal $(\varphi_{c,n} < \varphi_{c,\infty})$


$$p_n = (2\pi m)^{3/2} (kT)^{-1/2} v^3 \exp \left[- (\varepsilon_v - \varepsilon_{c,n}) / kT \right]$$

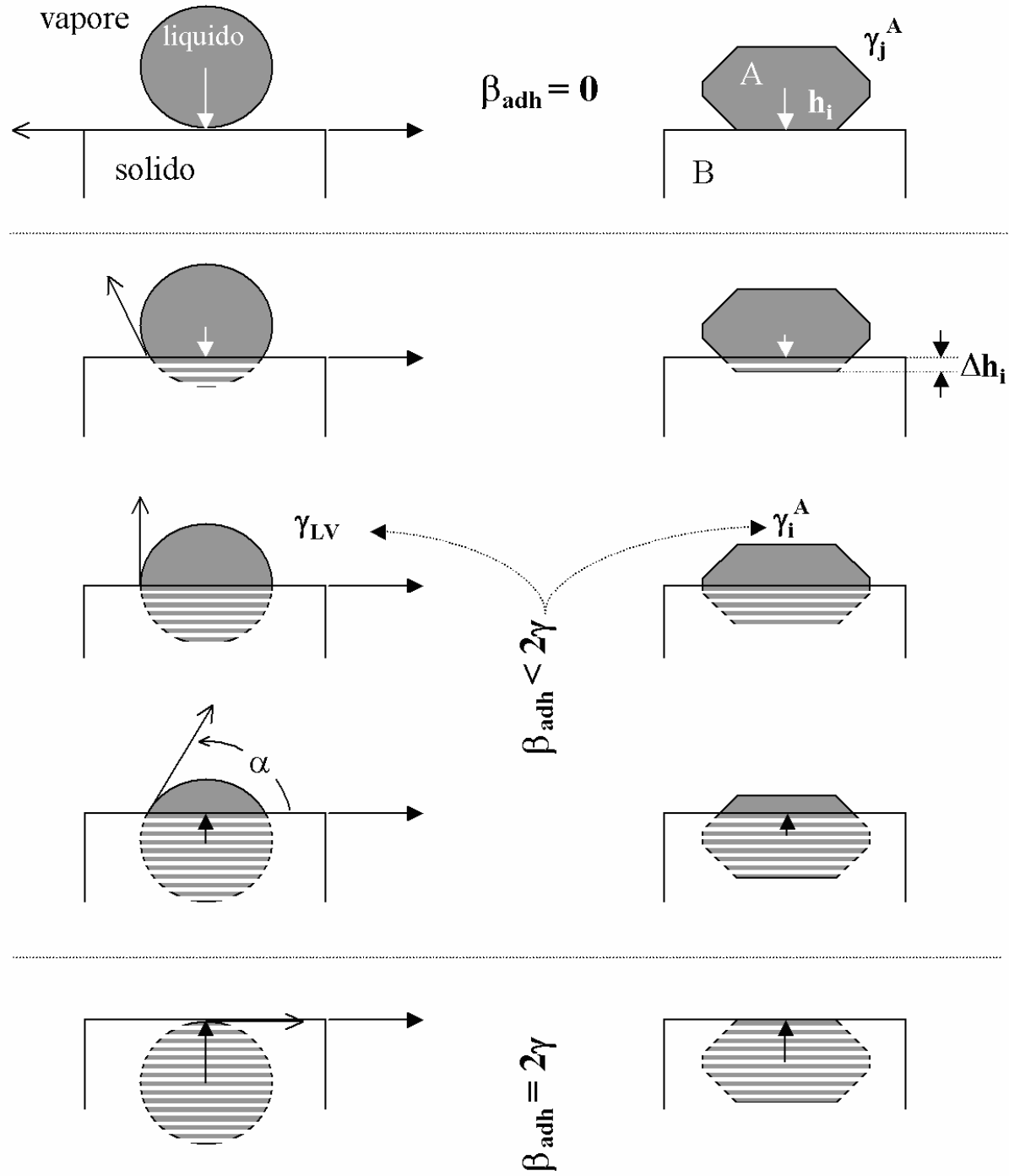


$$p_n \neq p_\infty$$

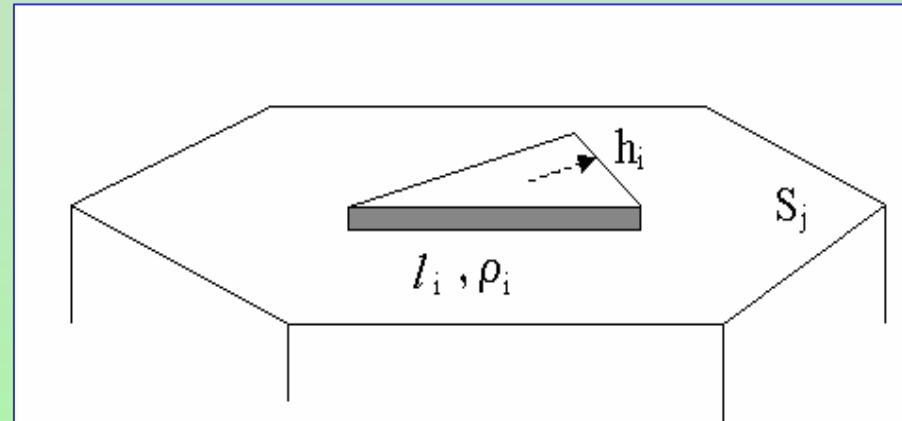
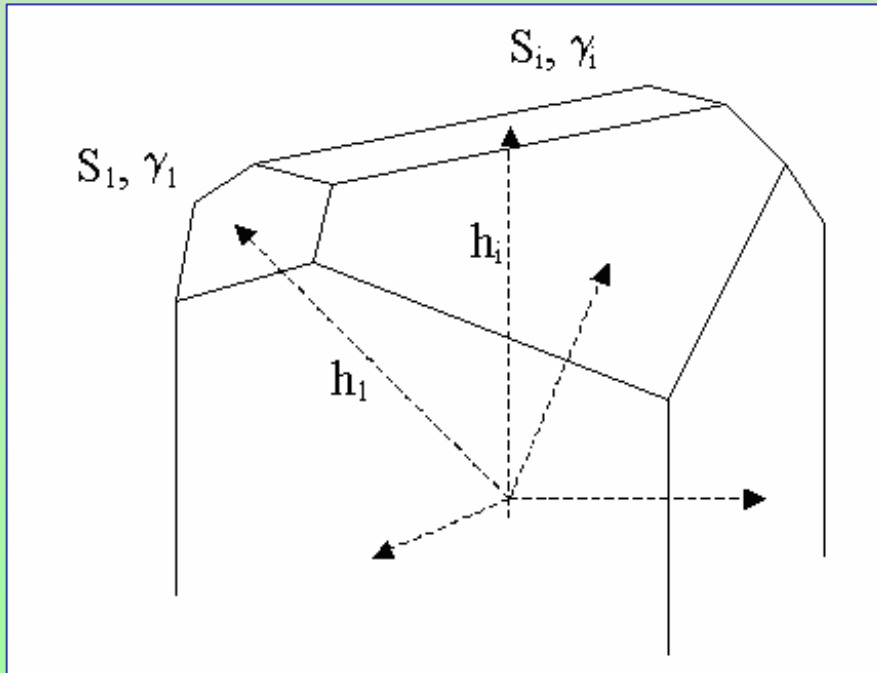
$$\Delta\mu = \mu - \mu_{\text{eq}} = kT \ln (p_n/p_\infty) = \varphi_{c,\infty} - \varphi_{c,n}$$

that is the master equation for equilibrium
of a finite crystal phase

- it follows that:
- - an **infinite** crystal is in equilibrium with its **saturated** vapour
- - a **finite** crystal is in equilibrium with its **supersaturated** vapour

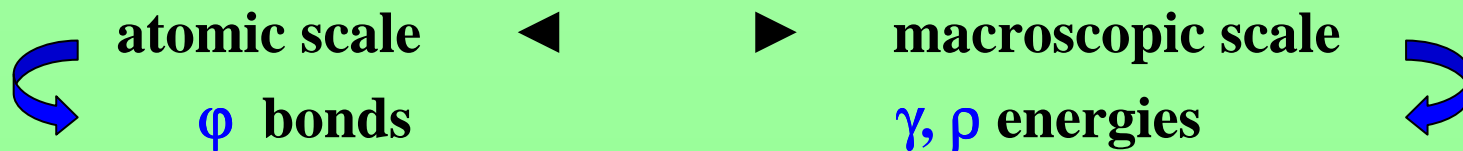


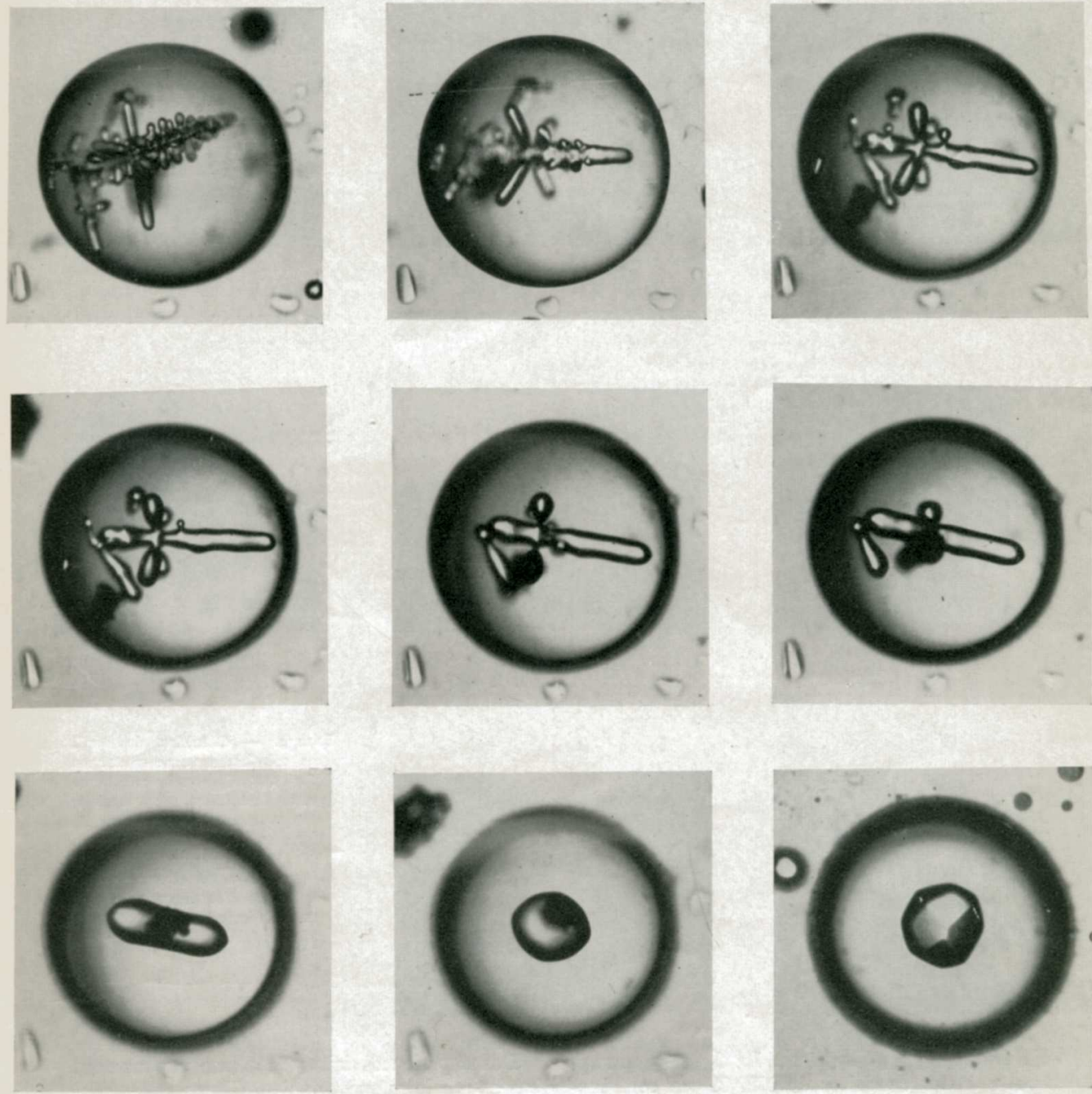
- The shape of crystals (3D – 2D) at equilibrium is **the most inner convex polyhedron**



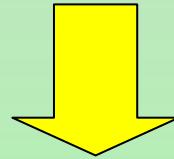
$$\frac{\gamma_i}{h_i} = \frac{\gamma_j}{h_j} = \frac{\gamma_k}{h_k} \dots = \text{constant} = \frac{\Delta\mu}{2\Omega}$$

Wulff' s theorem





The strong bonds between equilibrium and kinetics



The main roles played by the
equilibrium quantities
surface (γ) and edge (ρ) specific energies
in the *crystal growth* phenomena

♣ **3D nucleation frequency** (hetero-/ homogeneous)

$$J_{3D} = K_{3D} \exp \frac{- f \Omega^2 \gamma^3}{(kT)^3 (\ln \beta)^2}$$

Langmuir adsorption

$$\Delta\gamma = kT a^{-2} \ln(1 - \theta_{ads})$$

Growth rate of a flat face

perfect

$$R_{\text{mononuclear}} \approx J_{2D}$$

$$R_{\text{polynuclear}} \approx J_{2D}^{1/3}$$

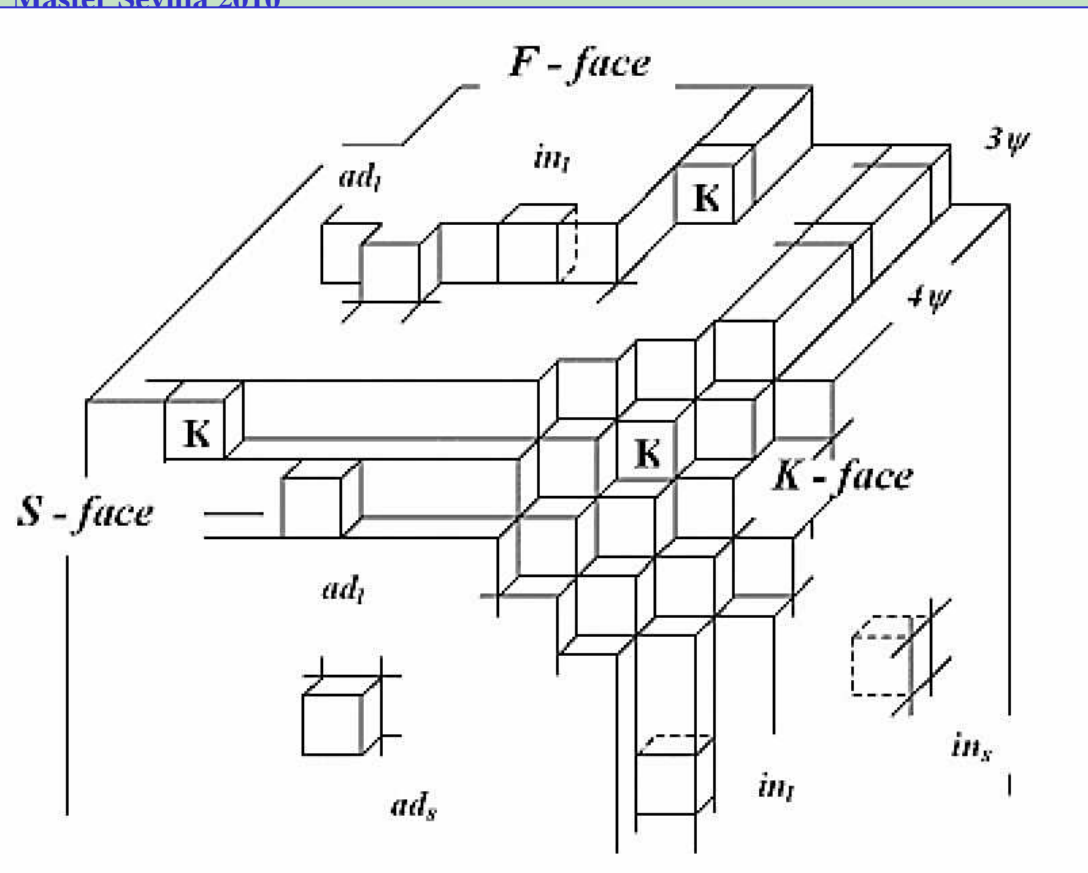
$$J_{2D} = K_{2D} \exp \frac{-fa^2 \rho^2}{(kT)^2 \ln \beta}$$

imperfect

$$R_{\text{spiral}} = v_{\text{train}} \times h / y_0 \quad \text{where} \quad y_0 \approx r^* = \frac{f' a_m^2 \rho}{(kT) \ln \beta}$$

Equidistance among train steps

The *growth mechanisms* of the
different kinds *of crystal faces*



Values for $\psi_1 = 4kT$
 (gold crystal near the
 melting point)

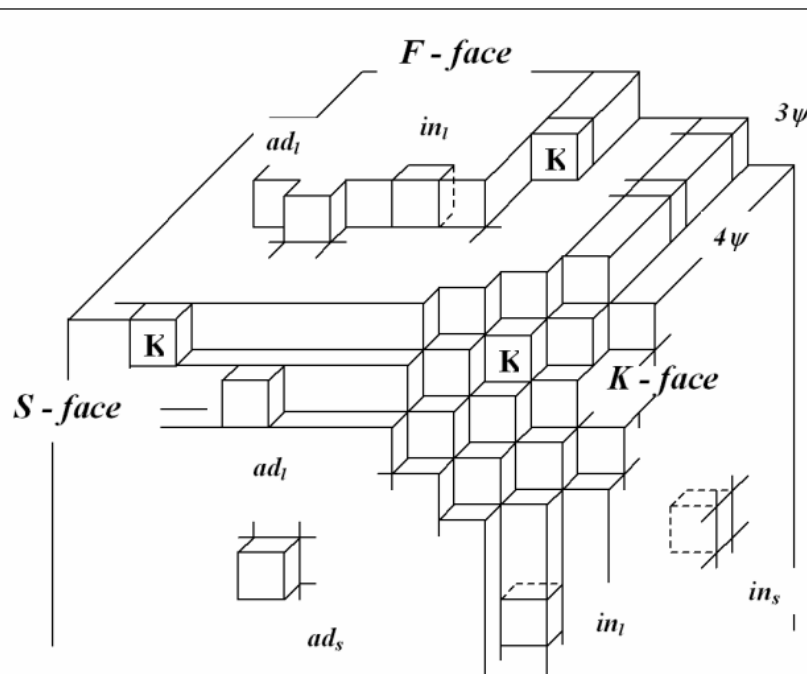
The kink position is
unique
 ... one half filled and one
 half empty...

Type of surface site	Separation work	Coverage degree θ_i	Exchange frequency s^{-1}
$ad_{surface}$	ψ_1	0.0003	3.06×10^7
ad_{ledge}	$2\psi_1$	0.0180	3.02×10^7
kink	$3\psi_1$	1/2	1.54×10^7
in_{ledge}	$4\psi_1$	0.9820	5.55×10^6
$in_{surface}$	$5\psi_1$	0.9997	1.03×10^4

The growth rate of a **kinked (K) face**

1

$$\frac{dN}{dt} = \frac{dn}{dt} \downarrow - \frac{dn}{dt} \uparrow \longrightarrow \frac{dN}{dt} = \frac{dn}{dt} \left(1 - \frac{\left(\frac{dn}{dt}\right)_{out}}{\left(\frac{dn}{dt}\right)_{in}} \right)$$



$$k_{eq} = \frac{\left(\frac{dn}{dt}\right)_{out}}{\left(\frac{dn}{dt}\right)_{in}} = \exp\left(\frac{-\Delta\mu}{kT}\right)$$

then

$$\frac{dN}{dt} = \frac{dn}{dt} \downarrow \left[1 - \exp\left(\frac{-\Delta\mu}{kT}\right) \right]$$

the net flow depends:
 on the **incoming flow** of particles,
 on **temperature** and
 on the **supersaturation**

calculating the **incoming flow.....**

◆ Evaluating the **flow incoming** on a face (Knudsen problem)

- a mono-atomic gas
- a hole of size a^2



$$\frac{dn}{dt} \downarrow = a^2 (2\pi mkT)^{-1/2} p$$

◆ a supersaturated vapour  $\Delta\mu = kT \ln \left(\frac{p}{p_{eq}} \right) = kT \ln \left(\frac{p_{eq} + \Delta p}{p_{eq}} \right)$

consequently $1 - \exp(-\Delta\mu/kT) = \left(\frac{\Delta p}{p} \right)$

◆ summing up : $\frac{dN}{dt} \downarrow = \frac{dn}{dt} \downarrow \left(\frac{\Delta p}{p} \right) = a^2 (2\pi mkT)^{-1/2} \Delta p$

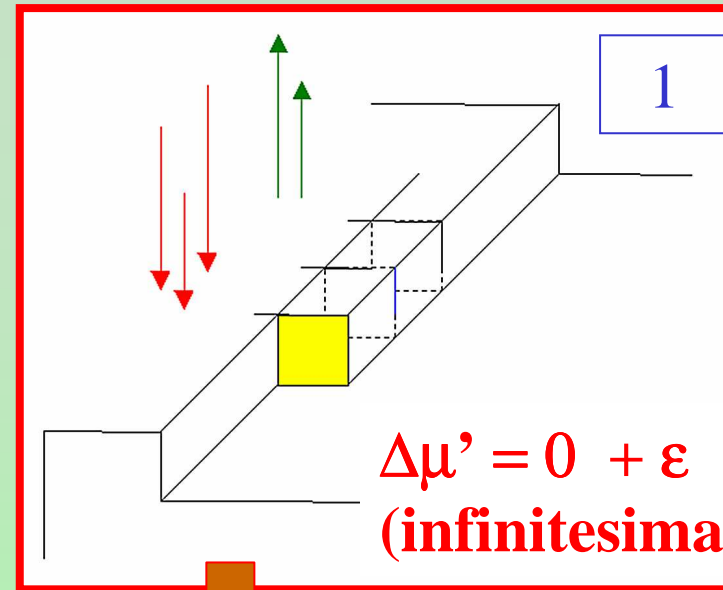
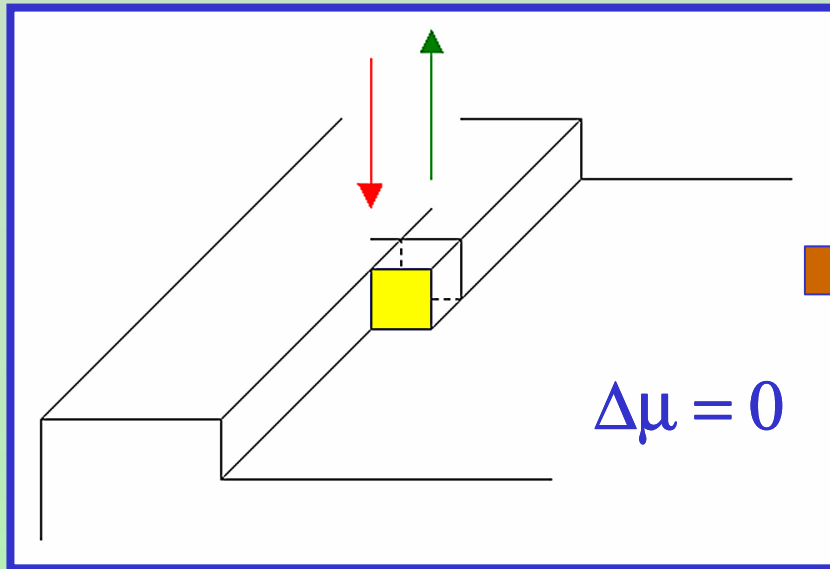
remembering that $\Delta p = p_{eq} \sigma$, the normal growth rate for a K face reads:

$$\mathbf{R_K} \approx \mathbf{d_{hkl}} a^2 (2\pi mkT)^{-1/2} \times \sigma = \mathbf{b_K} \times \sigma$$

The growth rate of a **flat (F) face**:

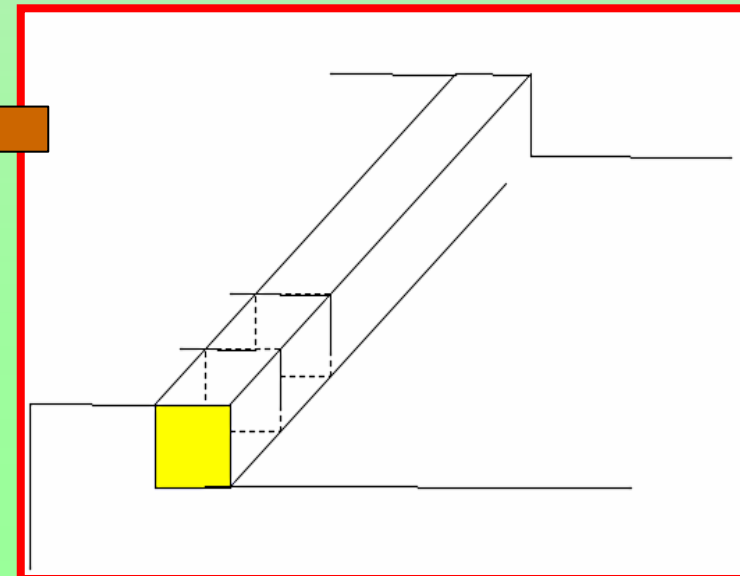
a) - perfect face

b) - defective face (crossed by screw dislocations)



* the **step** can be filled and hence **stops growing** unless $\Delta\mu' > \epsilon$ makes stable the adsorbed sites on the ledge

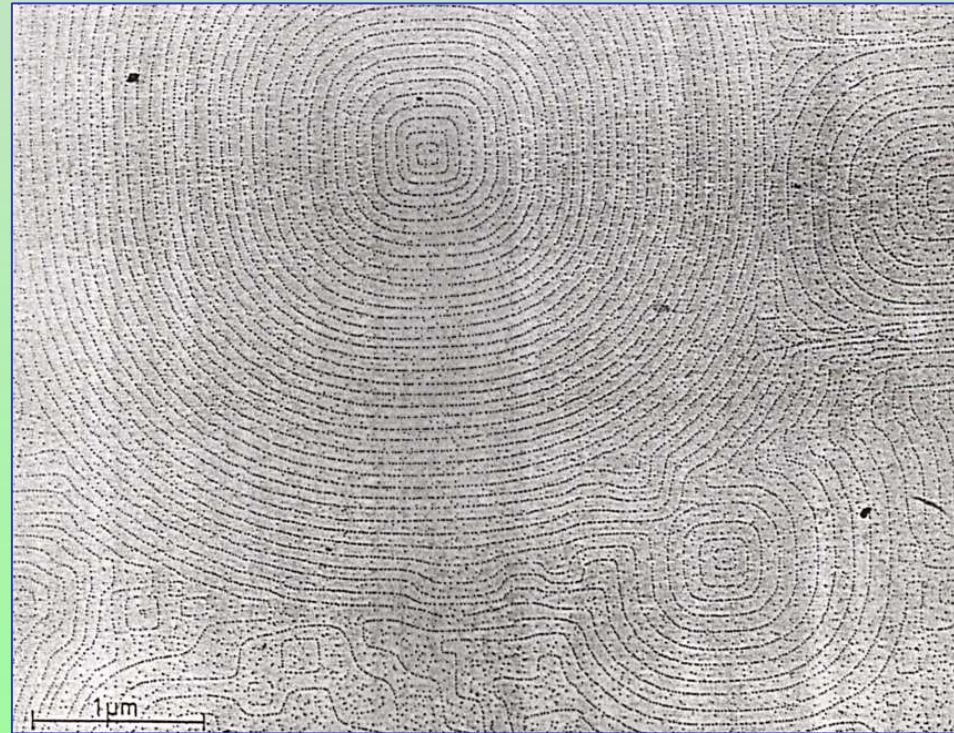
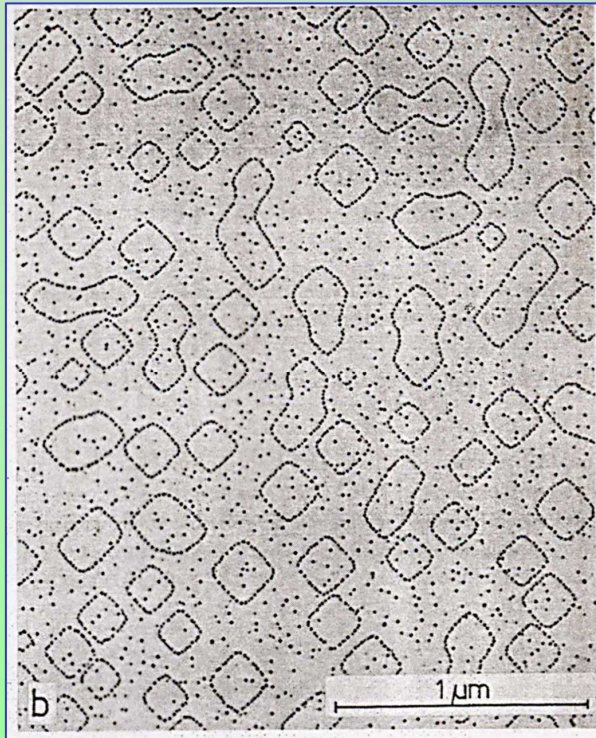
** the step advances and stops at the end of its face **new steps are needed**



2D nucleation

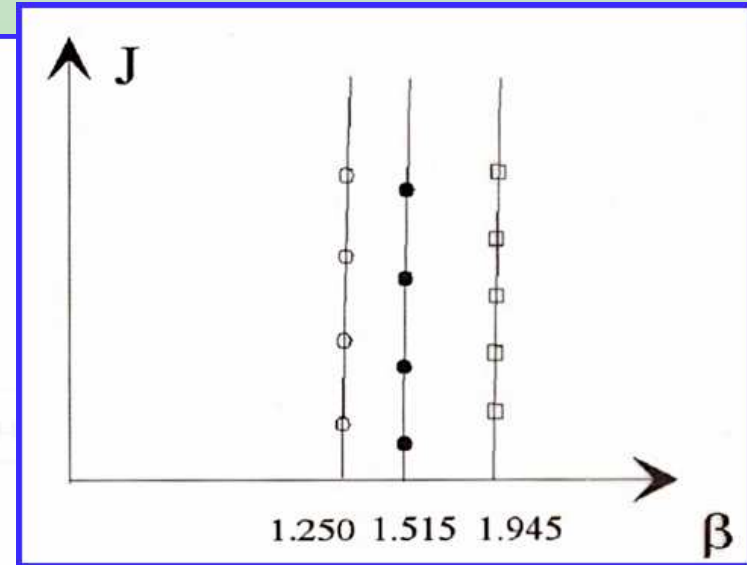
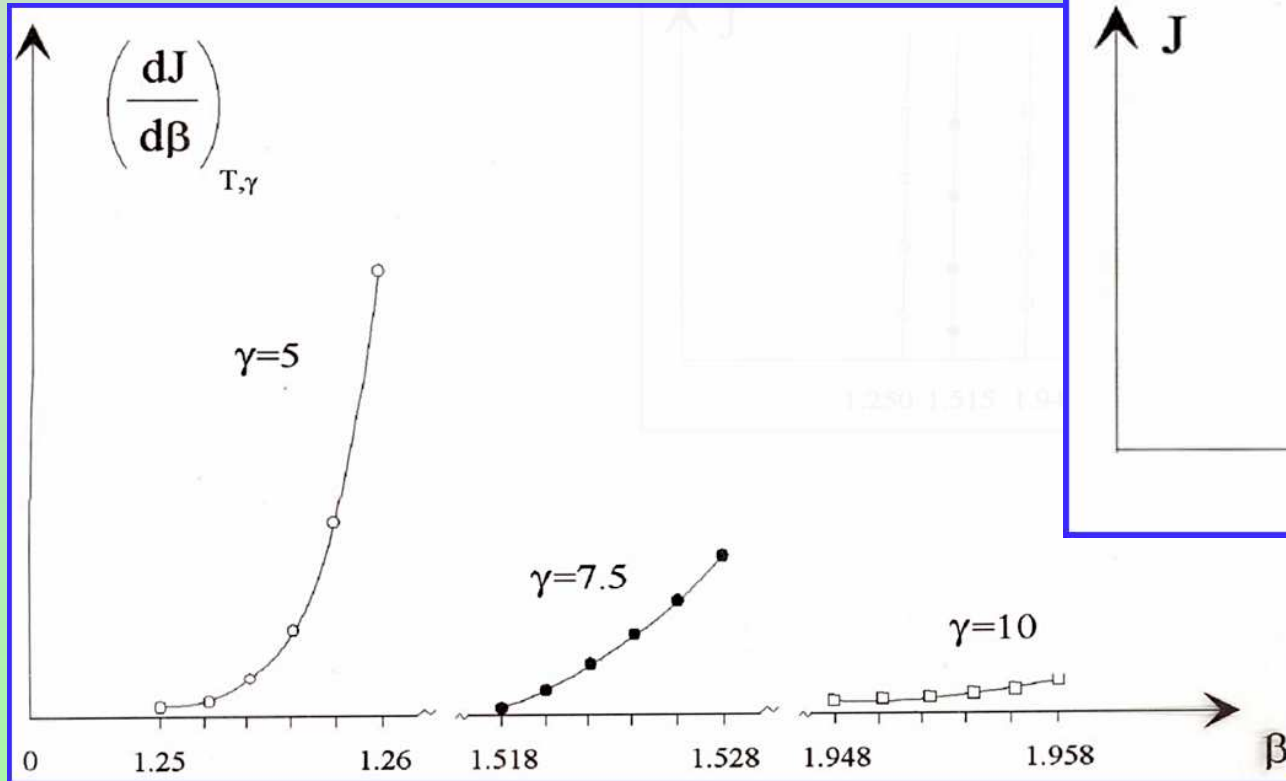
2D nuclei can form on a perfect face

- either randomly,
- or repeatedly, at the outcrop of an edge dislocation



Two parameters determine the **size** of a 2D nucleus and its **occurrence probability**:

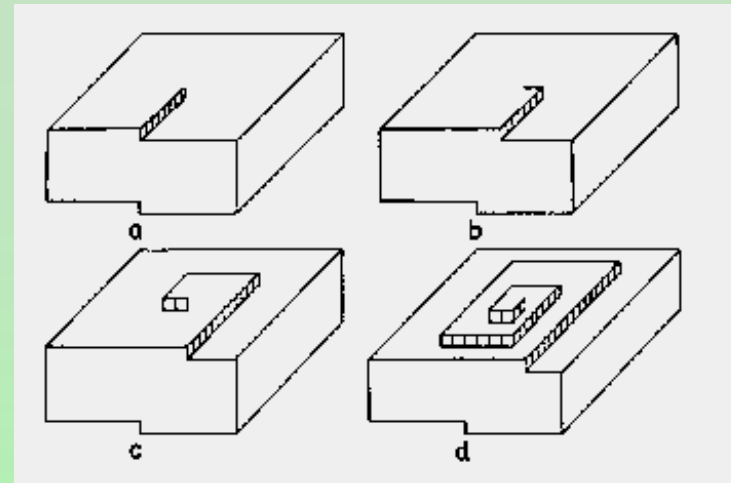
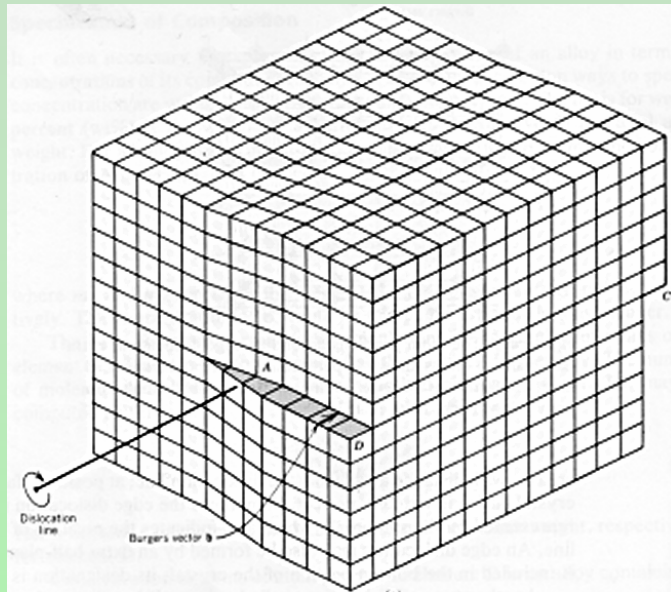
- the edge free energy ρ_{uvw}
 - the supersaturation $\Delta\mu$
- the activation energy for 2D nucleation



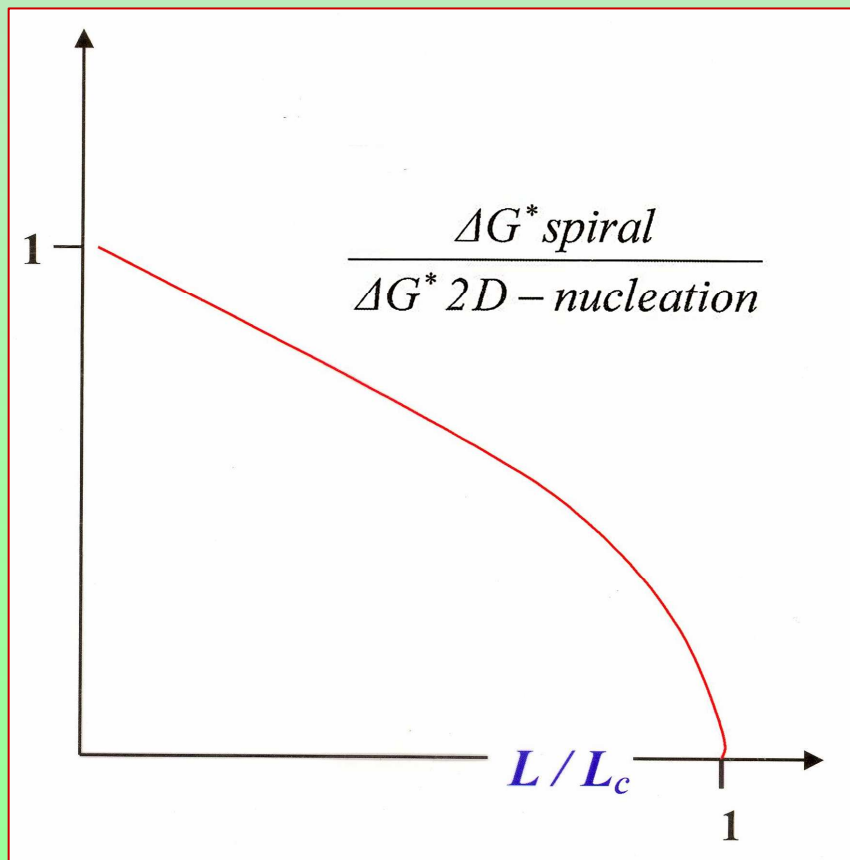
- The **nucleation frequency** (3D – 2D)
- and its **derivative**

as a function of the **surface energy γ**
and of the **supersaturation β**

From the screw dislocations to the growth spirals



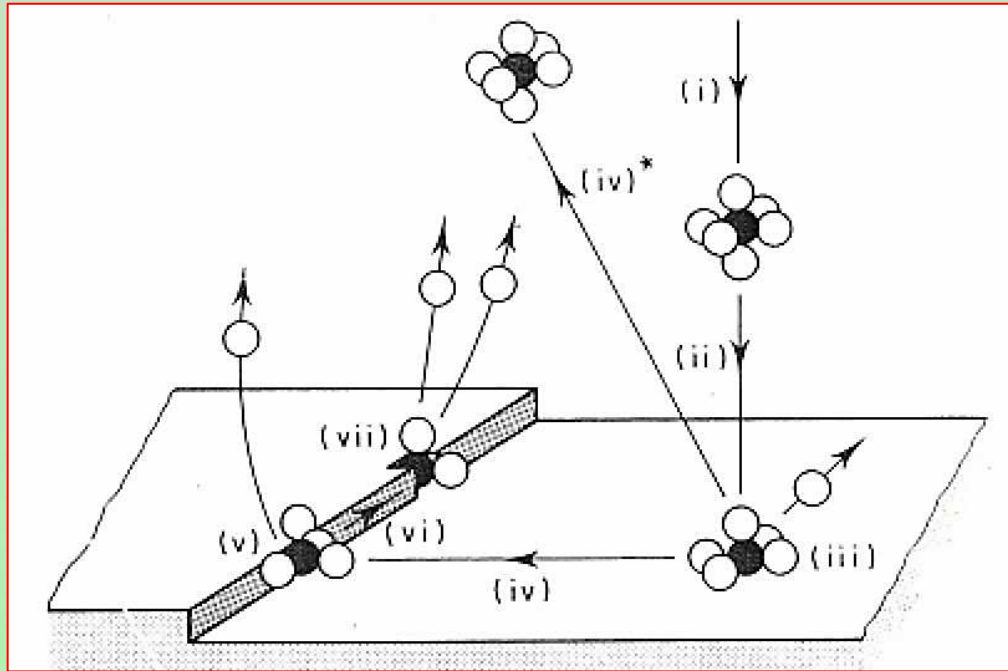
The **activation energy for spiral growth** reduces to zero once the length of the exposed ledge of the screw dislocation reaches the size of the 2D nucleus compatible with the bulk supersaturation
(the exposed ledges generally fulfil this condition)



- **exposed ledge** (critical length)
- **the activation energy** for step advancement is a function of the length of the exposed ledge

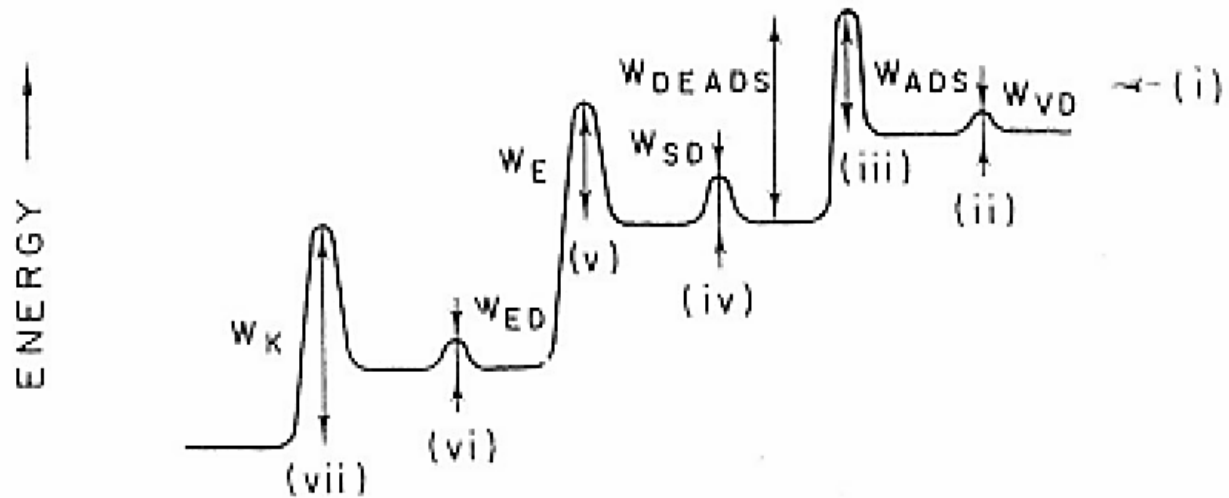
- * Miers : moving steps (1903-1904)
- * Heck : spirals on paraffin crystals (1937)
- * Burgers : screw dislocation (1939)
- * Griffin : spirals on beryl (1951)

BCF (1951) \longrightarrow **spiral growth theory**

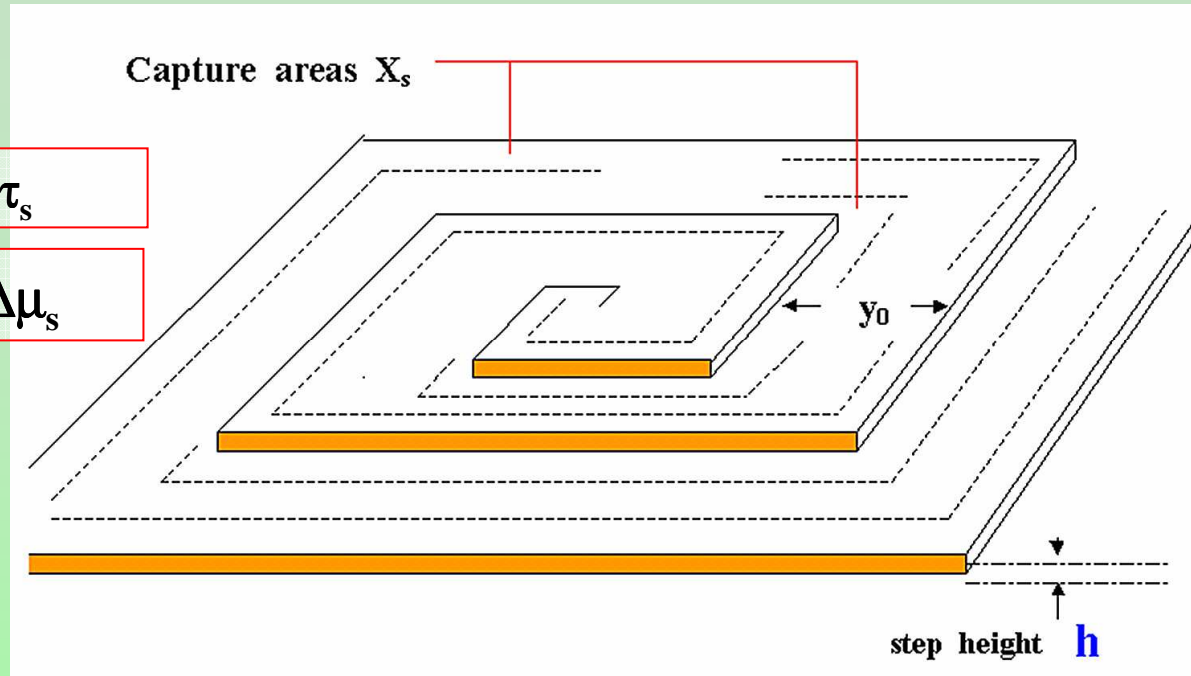


The events leading to crystal growth: diffusion in the volume, on the surface, along the step, to the kink with integration; desolvation; desorption

To each of these processes corresponds an activation energy of different magnitude



Spiral : the growth parameters (surface diffusion model)



$$x_s^2 = D_s \tau_s$$

$$y_0 \approx r_{2D}^* = \rho a^2 / \Delta \mu_s$$

the normal rate of the spiral

$$R_{sp} = h \times \mathbf{V}_{train} / y_0$$

- Transport phenomena** (out of the boundary layer)
- Diffusion** (bulk, surface, ledges)
- Kink density of the steps**
- Interface phenomena** (relaxation time for desolvation....)
- Supersaturation** $\Delta \mu$

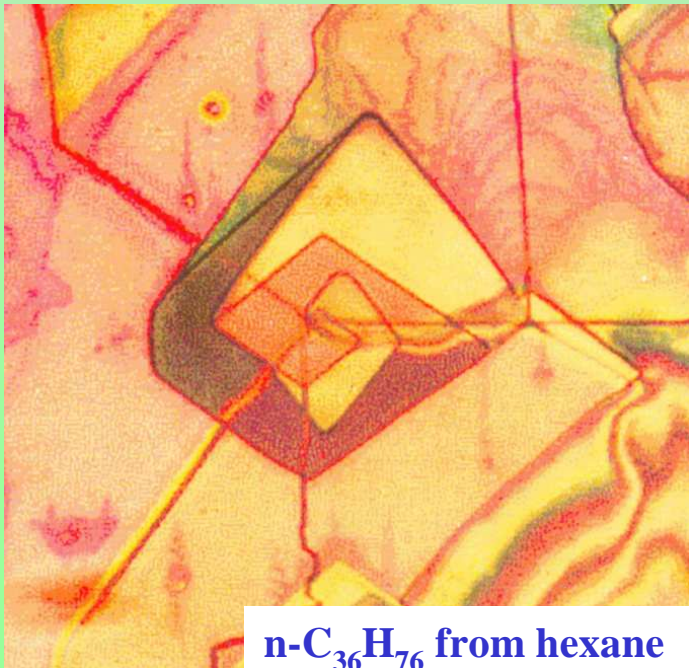
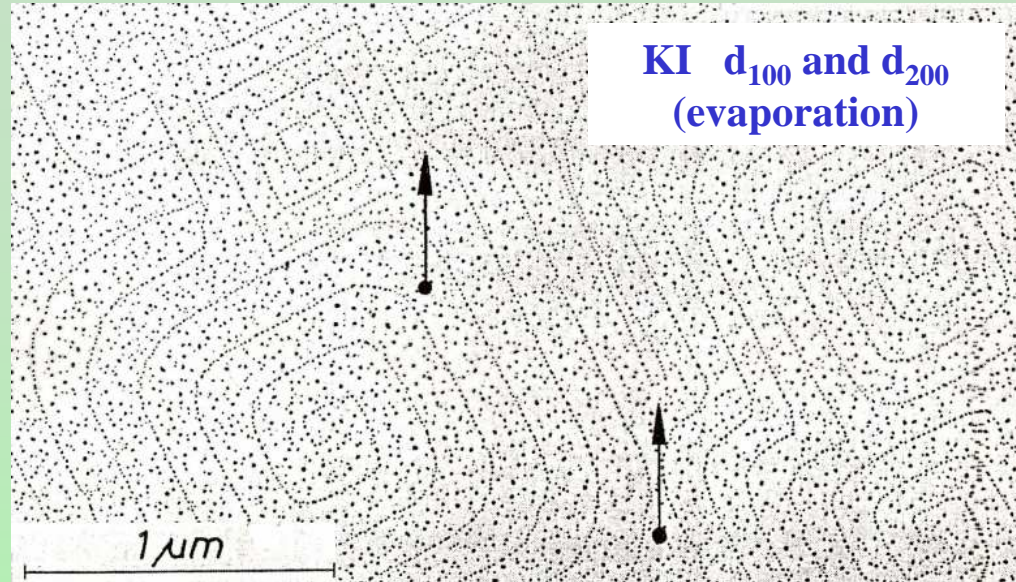
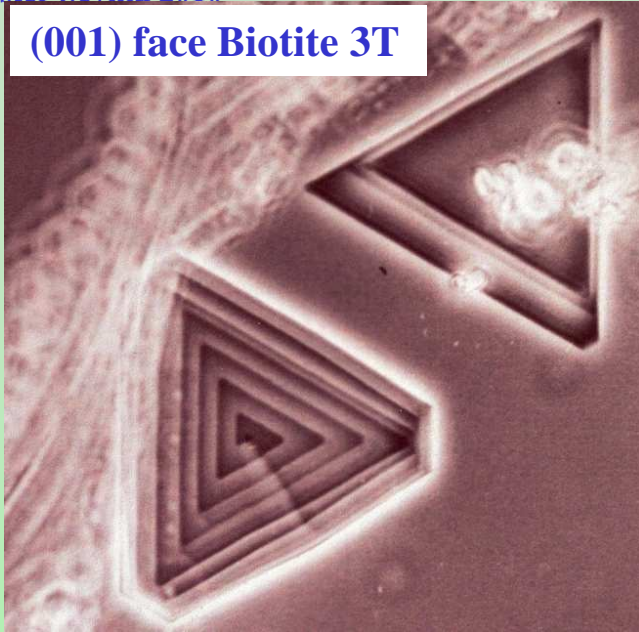
**When the surface diffusion cannot be neglected
(vapour and solution growth)**

BCF model for surface diffusion (1951)

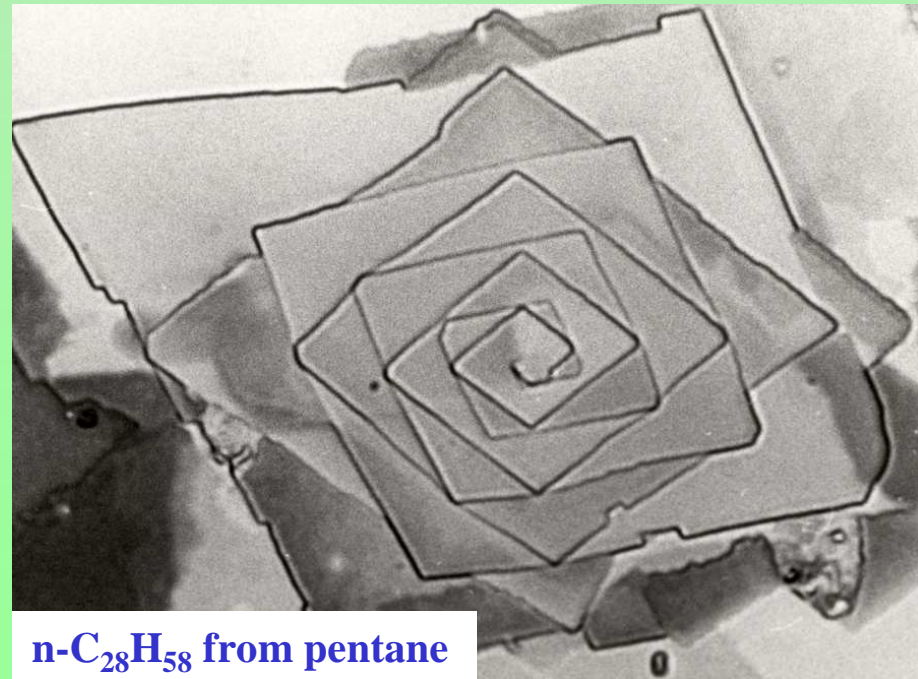
Evaluating the advancement rate of a **spiral step train:**

- **first, the velocity of a **single step** has to be evaluated**
- **secondly, the role played by the step equidistance (y_0) has to be considered, since determines the spiral **“slope”****

(001) face Biotite 3T



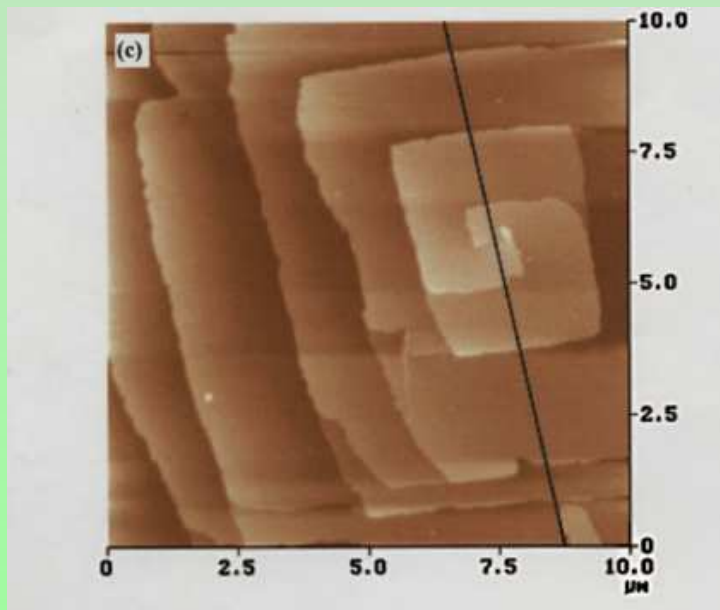
$n\text{-C}_{36}\text{H}_{76}$ from hexane



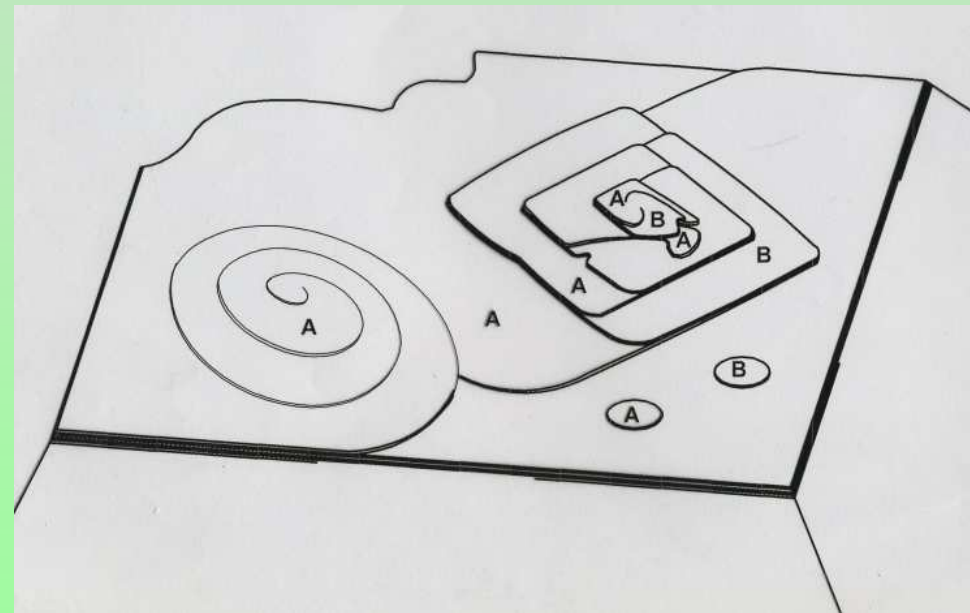
$n\text{-C}_{28}\text{H}_{58}$ from pentane

The spirals (both for growth and dissolution) reveal, better than the 2D nuclei:

- the **symmetry of the surface** on which the spiral develops
- the **inner structure of the crystal** involved in the exposed ledge at the outcrop of the screw dislocation



(001) α -amylase



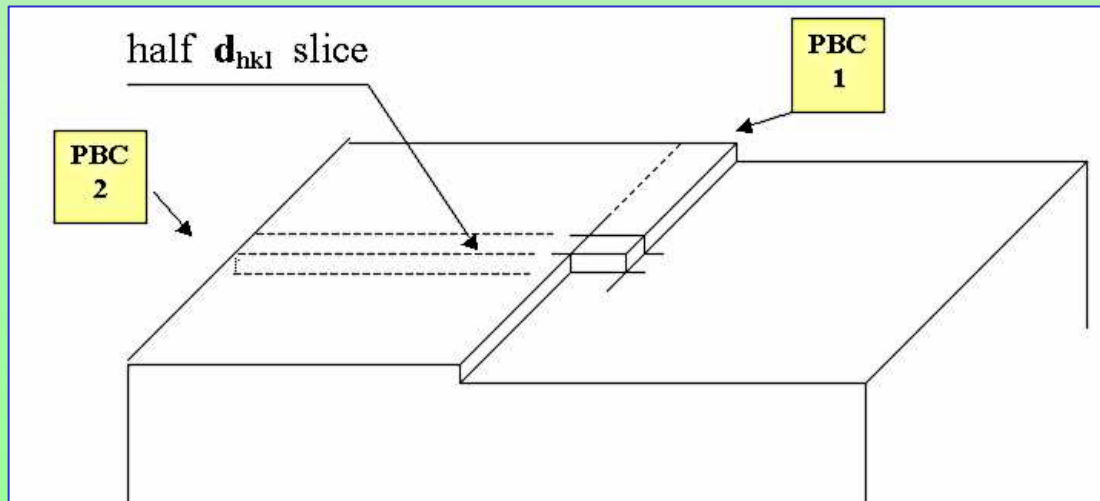
(001) α -amylase two polytypes in the same individual...

Predicting
the equilibrium and growth morphology
of crystals

The energy aspect of the Hartman –Perdok method (1955)

- **slices** with thickness d_{hkl} fulfilling the extinction rules
- the slice energy E_{slice}
- the attachment energy E_{att}
- the constancy property

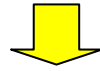
$$E_{\text{kink}} = E_{\text{att}} + E_{\text{slice}}$$



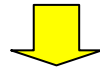
for a given crystal:
 when $E_{\text{slice}} \uparrow$ $E_{\text{att}} \downarrow$

$$R_{hkl} \approx E_{\text{att}}(hkl)$$

- Predicting the equilibrium shape of gypsum



- Searching for the “lowest surface energy” face profiles



the approaches to be followed

The PBC method (Hartman & Perdok, 1951)

- ♣ first neighbour bonds between growth units building the crystal
- ♣ periodic bond chains (non-polar)
- ♣ character of the faces (F,S,K)
- ♣ alternative surface profiles

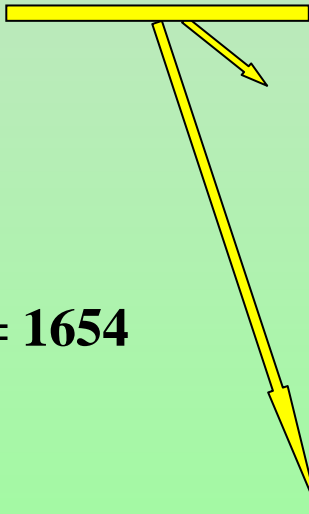
The method of the systematic – cuts (GDIS-Fleming & Rohl, 2005)

- ◆ Surface profiles are obtained irrespective of the face character
- ◆ The only constraints on the profiles are the electroneutrality and the annihilation of the dipole moment
- ◆ The number of possible profiles (for a given face) is higher than that obtained through the HP method

The surface energy ($\gamma \rightarrow \text{erg cm}^{-2}$) of a real crystal is affected by the “surface relaxation”

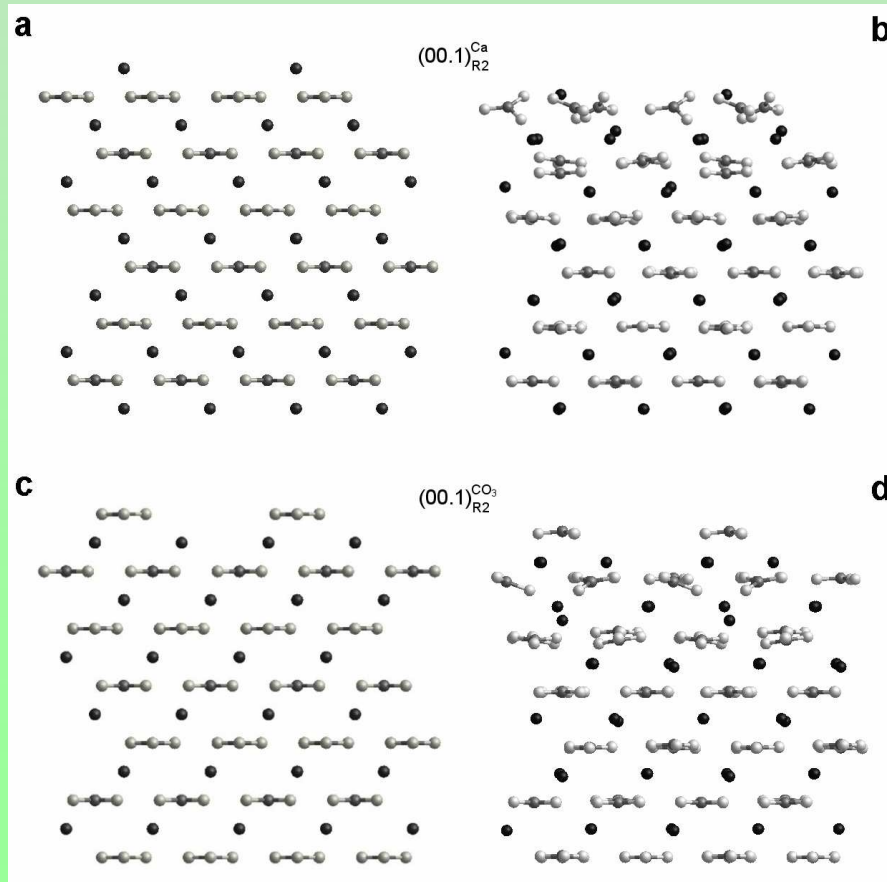
Calcite (0001) face

ideal



$$\gamma = 1654$$

$$\gamma = 1654$$



relaxed

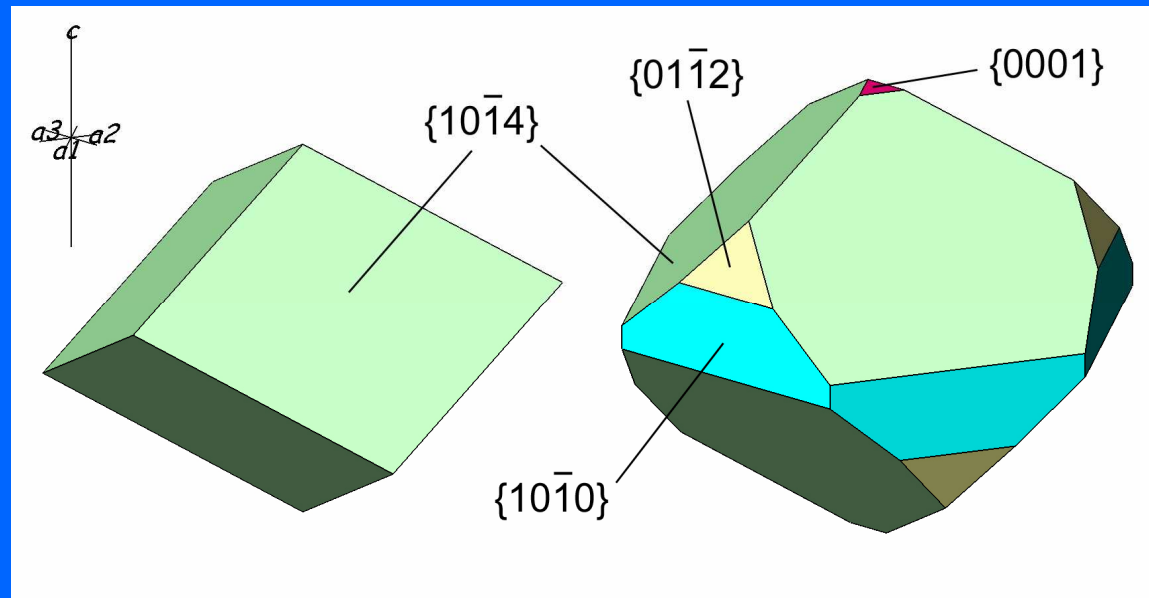
$$\gamma = 849$$

$$\gamma = 711$$

The equilibrium shape of calcite at the temperature of zero Kelvin

ideal surfaces

relaxed surfaces



Consequences: 1) - new faces for adsorption of solvent and impurities)
2) – the 3D nucleation frequency dramatically changes

GYPSUM

projected along the $[001]$ direction

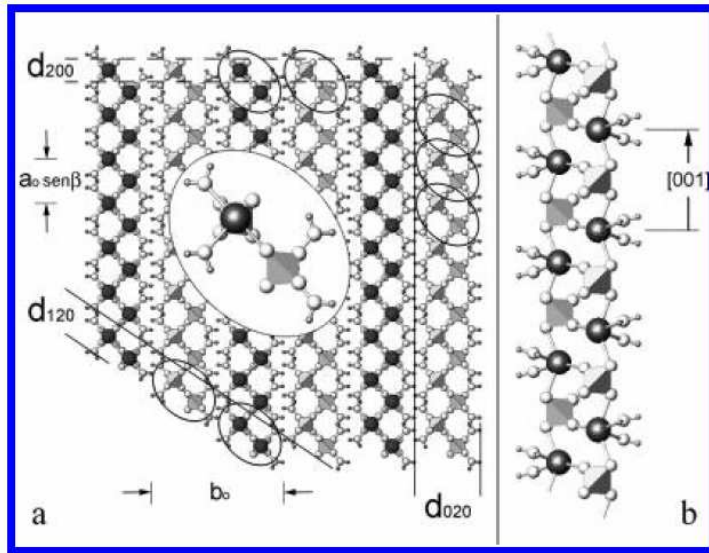


Figure 1. (a) Gypsum structure projected along the $[001]$ direction. The $[001]_a$ PBC allows one to draw the surface profiles of the $\{010\}_a$ and $\{120\}_a$ F-forms and of the $\{100\}_a$ S-form. (b) The development of the $[001]_a$ PBC showing the strong $\text{Ca}-\text{O}(\text{SO}_4^{2-})$ bonds between the polar $[001]$ chains.

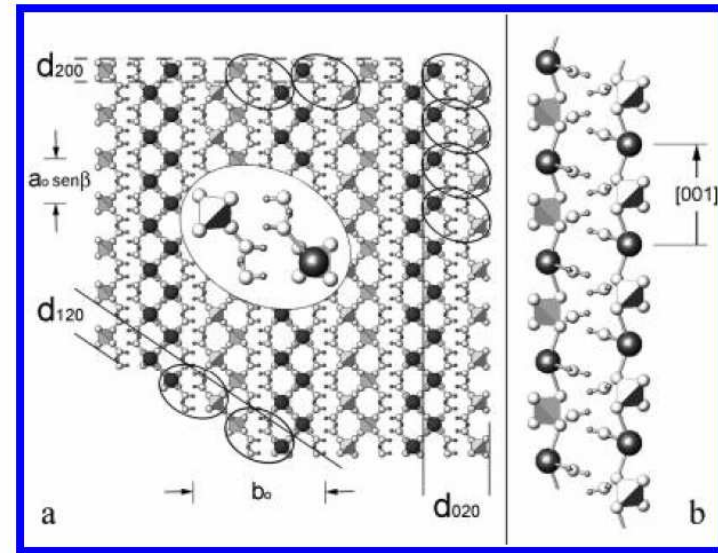
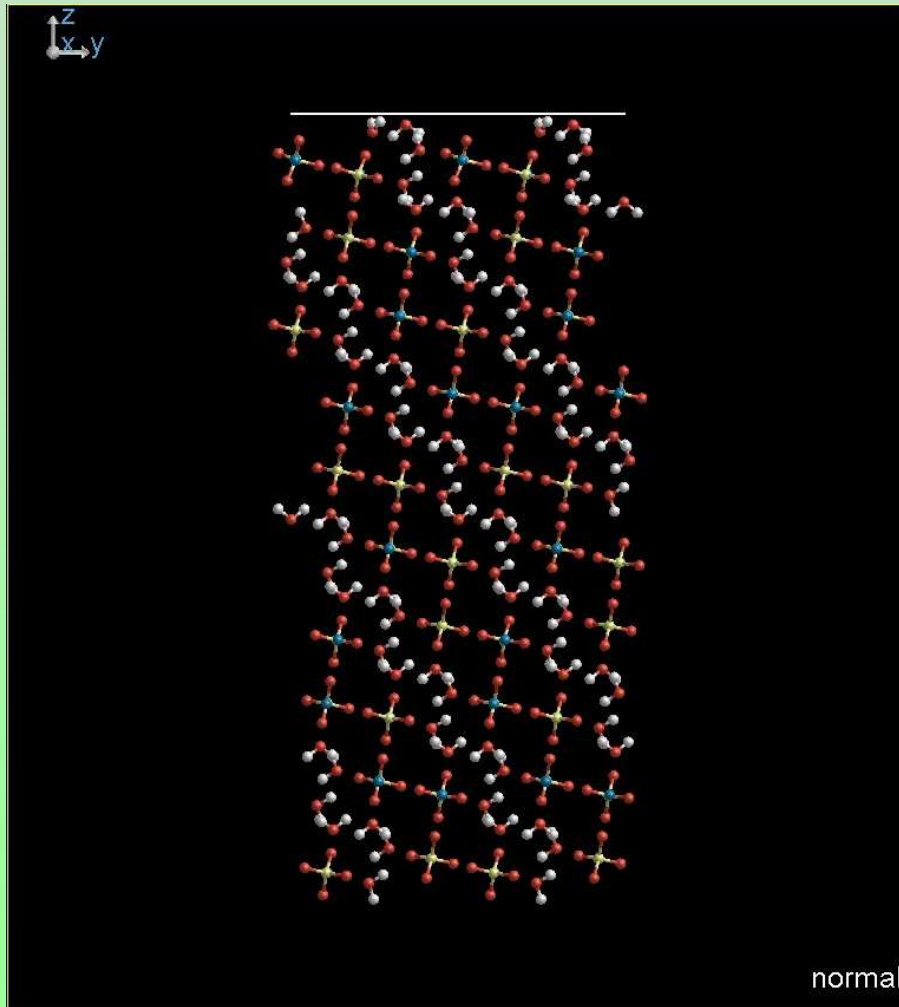
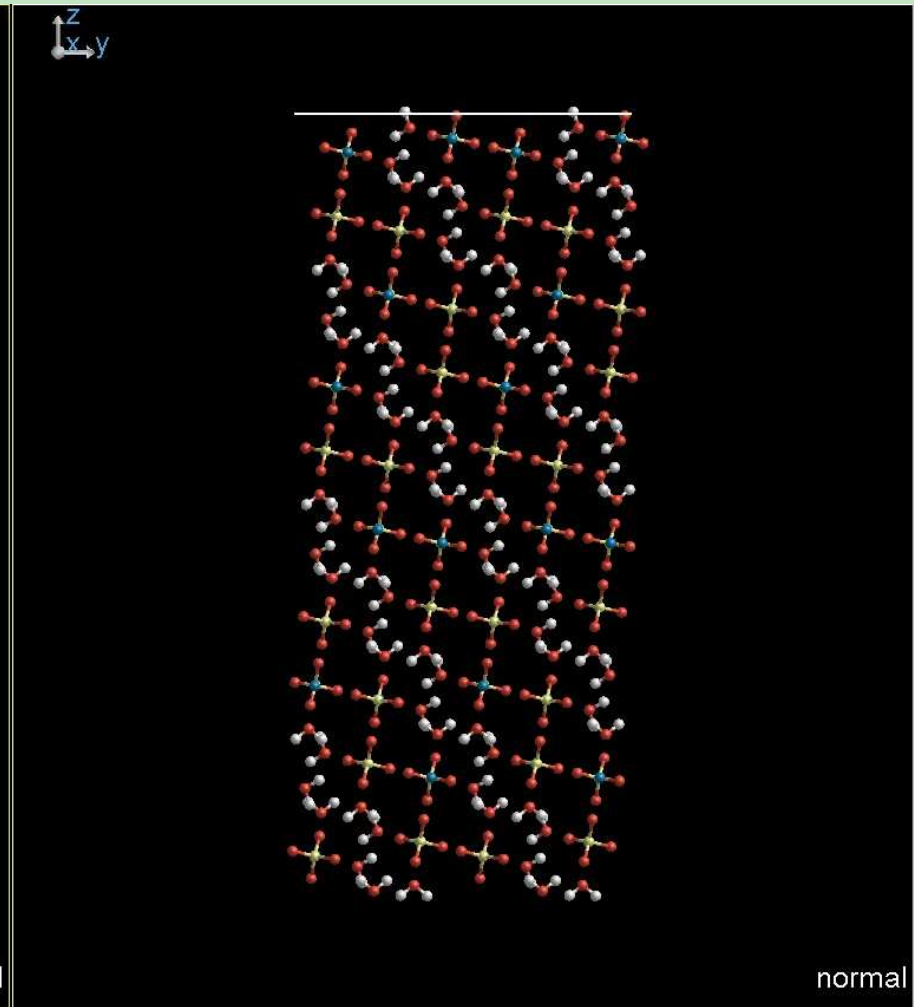


Figure 2. (a) Gypsum structure projected along the $[001]$ direction. The $[001]_b$ PBC allows one to draw the surface profiles of the $\{010\}_b$ and $\{120\}_b$ F-forms and of the $\{100\}_b$ S-form. (b) The development of the $[001]_b$ PBC showing the hydrogen bonds ($\text{O}_w-\text{H}\cdots\text{O}(\text{SO}_4^{2-})$) between the polar $[001]$ chains.

Gesso Faccia (120)



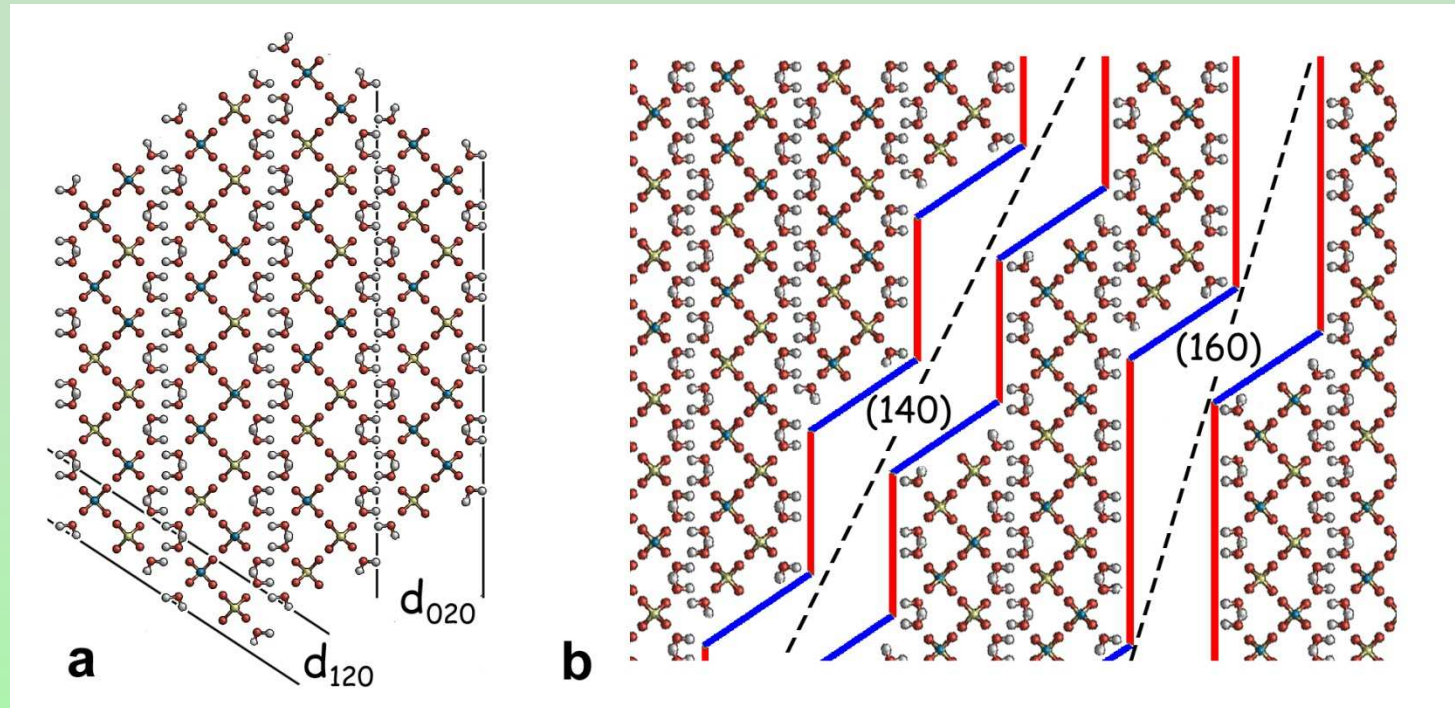
543 erg cm^{-2}



579 erg cm^{-2}

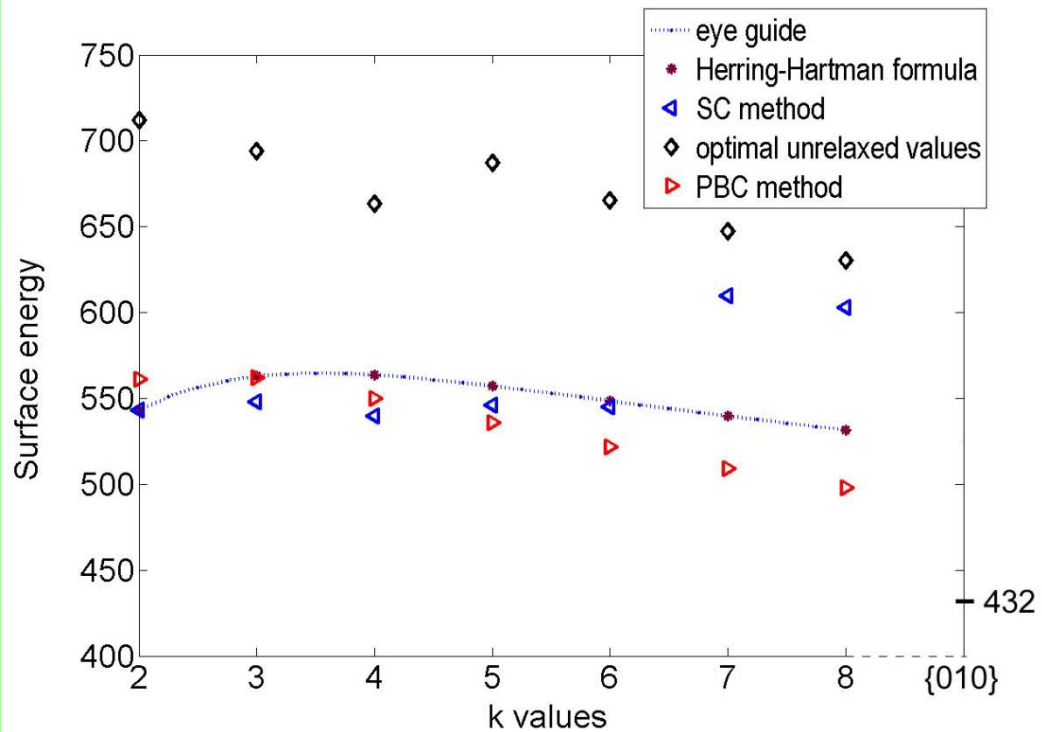
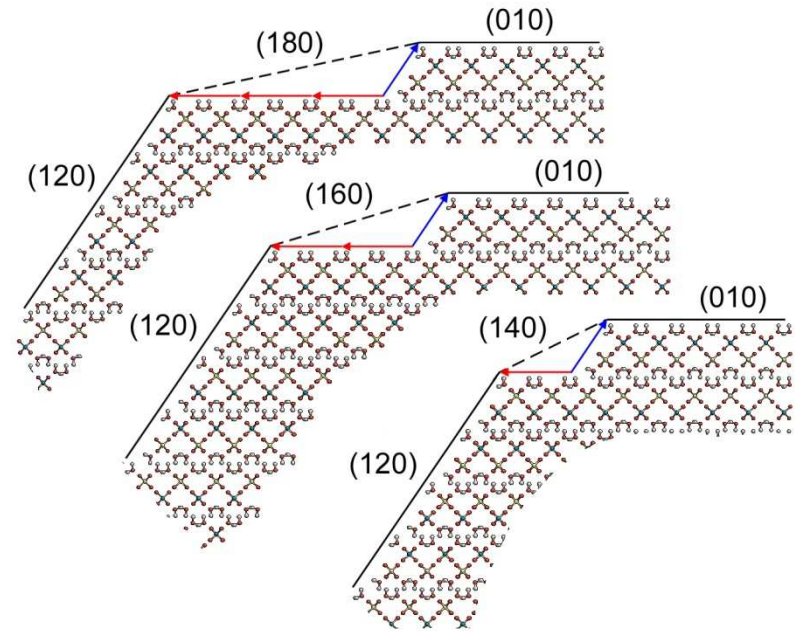
Gesso: energie specifiche di superficie (erg cm⁻²)

Form {hkl}	Growth mode	U _{PBC} unrelaxed	R _{PBC} relaxed	Δ _{UR} (%)	U _{SCM} unrelaxed	R _{SCM} relaxed	Δ _{UR} (%)	
{010}	F				463	432	-6.69	
		(a)	463	432	-6.69	796	503	-36.80
		(b)	1123	965	-14.07		752	-5.52
					1123	965	-14.07	
{120}	F				712	543	-23.73	
						579	-18.68	
		(a)	735	561	-23.67	763	621	-18.61
		(b)	763	621	-18.61	822	561	-31.75
						694	-15.57	
			888	702	-26.49			

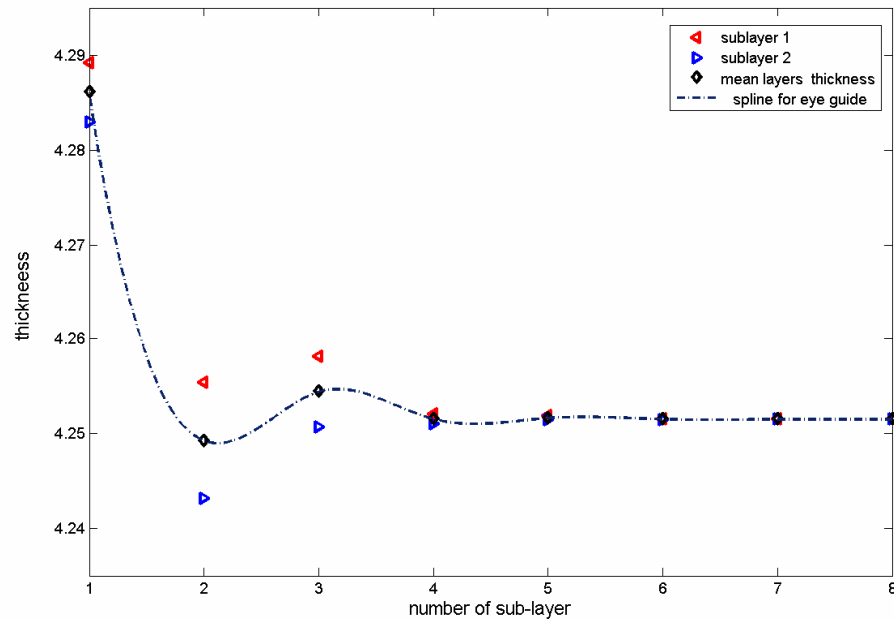


- (a) The unrelaxed profiles of the faces (120) and (010) of gypsum built by the PBC method. Both faces show F character. The repeatable thickness of the (010) face corresponds to one half of the [010] vector, owing to the systematic extinction rules.
- (b) The simplest way to draw the stepped profiles of the faces (140) and (160). The (140) profile is made by alternating the *minimum repeatable segments* $|\frac{1}{2}[2\ 0]|$ and $|[100] \sin\beta|$ of the faces (120) and (010), respectively. The segments, for the (160) profile, become $|\frac{1}{2}[2\ 0]|$ and $2 \times |[100] \sin\beta|$, respectively.

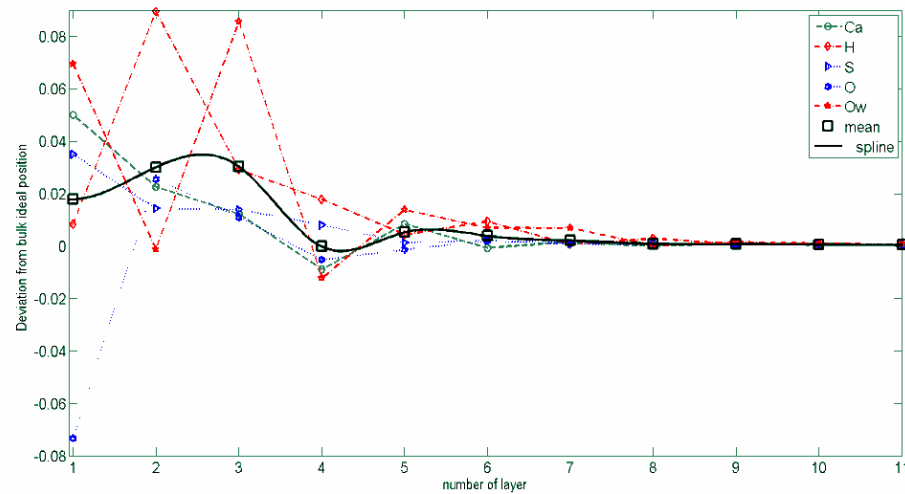
The composition of stepped $\{1k0\}$ surface profiles for even k values. Arrows indicate the length of the segments representing the elementary A_{120} (in blue) and A_{010} (in red) areas. Dotted lines stay for the areas related to the $\{1k0\}$ forms.



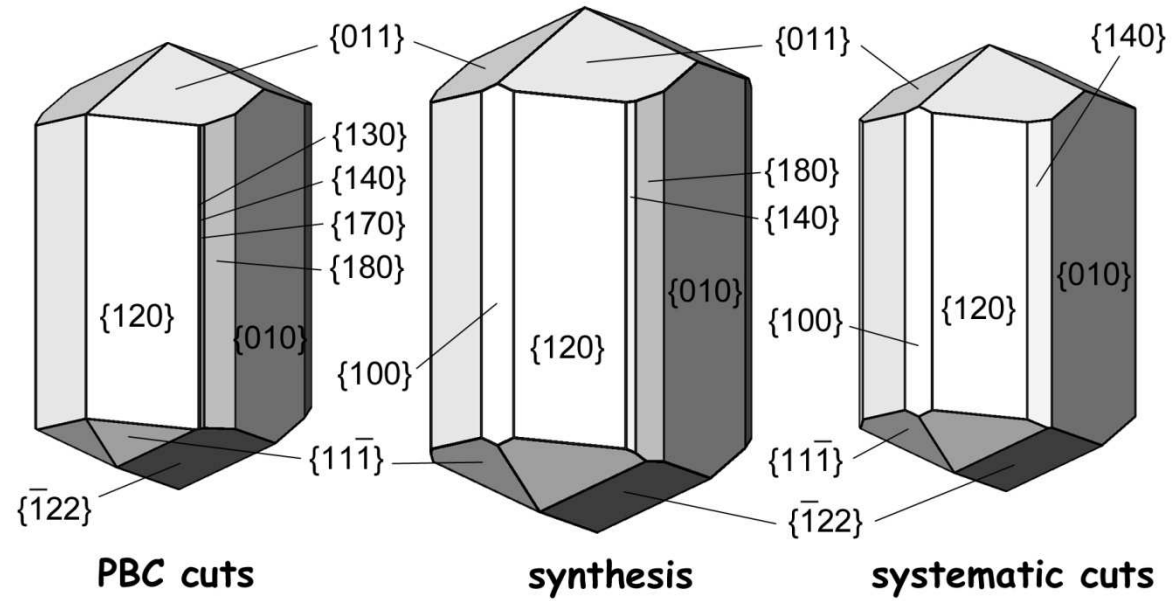
Surface energy of the S faces $\{1k0\}$ of gypsum crystal. Triangles shows the surface energy calculated from initial surface profiles obtained by the methods PBC and SC. Diamond are the optimal energies of the unrelaxed surface structure.



Deviation, from the bulk distance, between equivalent Ca layers measured along the perpendicular to the (120) surface.

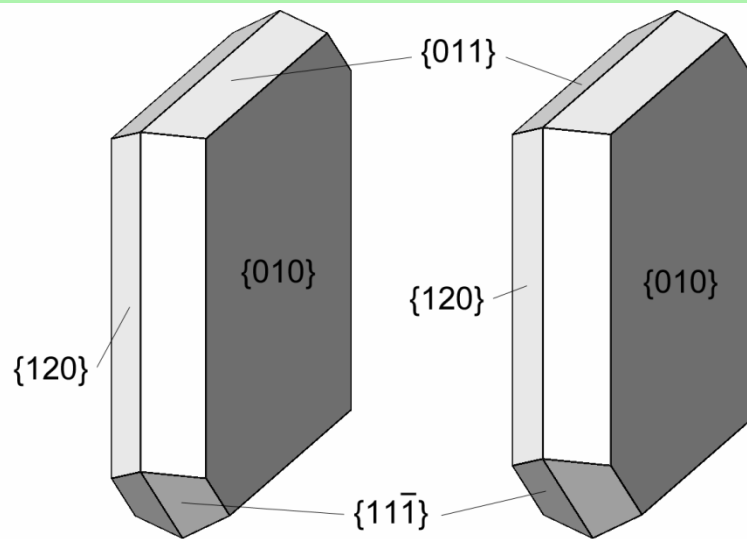


Surface (120) obtained with the SC method. Variation, in direction t^*_{120} , of the positions (Å) of the atomic sub-layers from the ideal positions in the bulk. The lines are a guide for the eye.



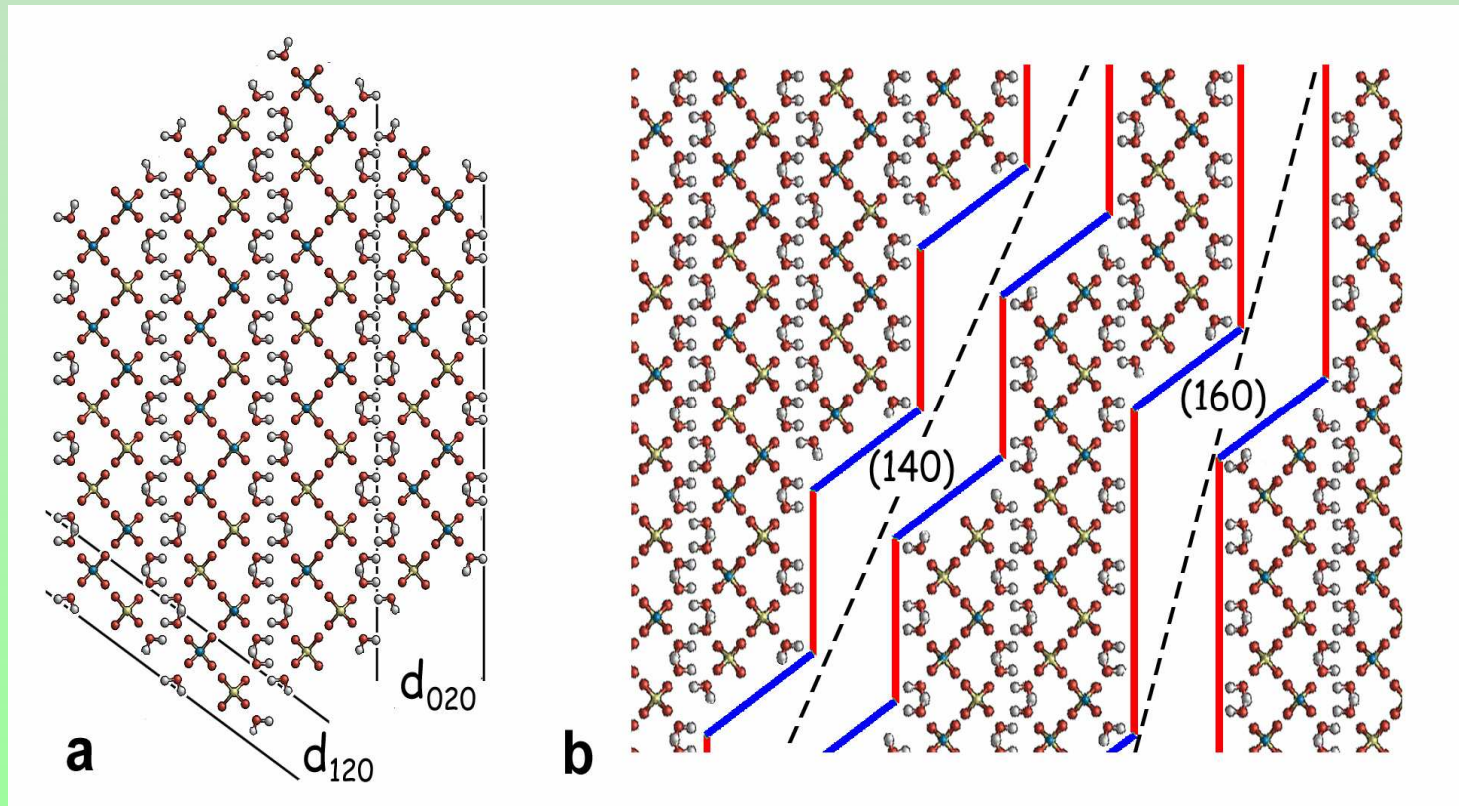
Equilibrium morphology

Un-relaxed growth morphology



Relaxed growth morphology

A model of the “best” surface profiles of the $\{1k0\}$ forms of gypsum



Calculating the **surface energy** of $\{130\}$, $\{140\}$, $\{150\}$, $\{160\}$, $\{170\}$ and $\{180\}$...

The surface energy value (γ_{xs}) we need when working in the system crystal / solution

from easy measurements

from molecular dynamics

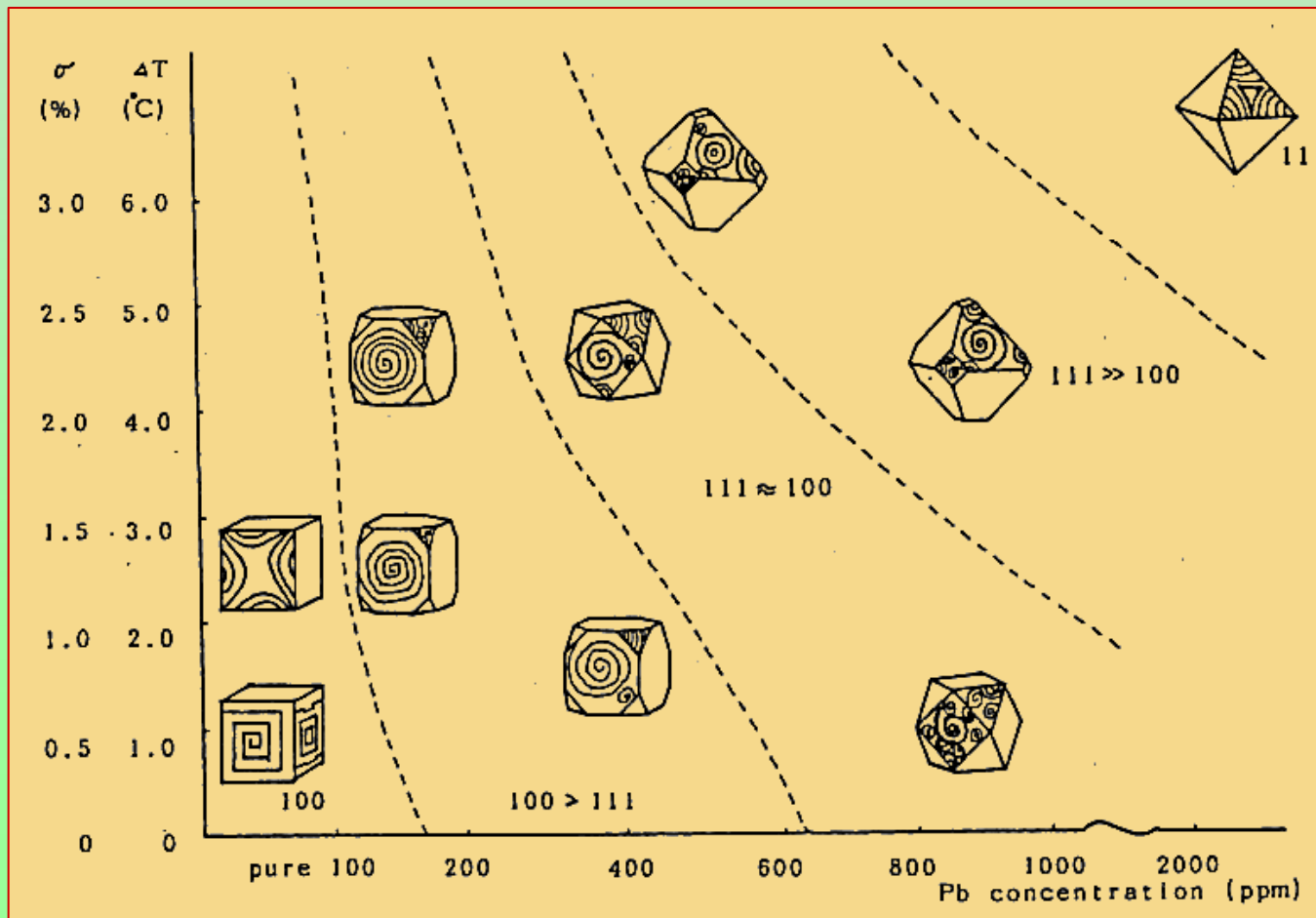
- $$\gamma_{xs} = \gamma_x + \gamma_s - \beta_{adh}$$

- where
$$\gamma_x = \gamma_x (T = 0 K) - T \times S$$

from *ab initio* calculation or
from semi-empirical potential

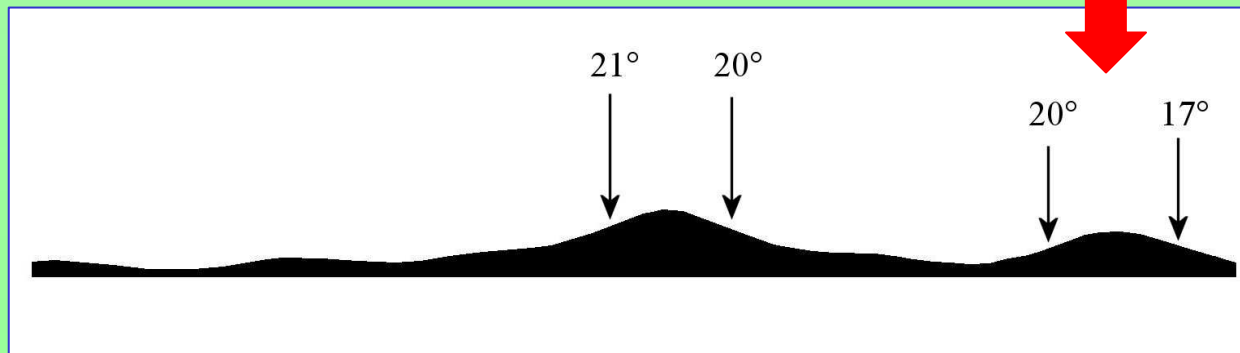
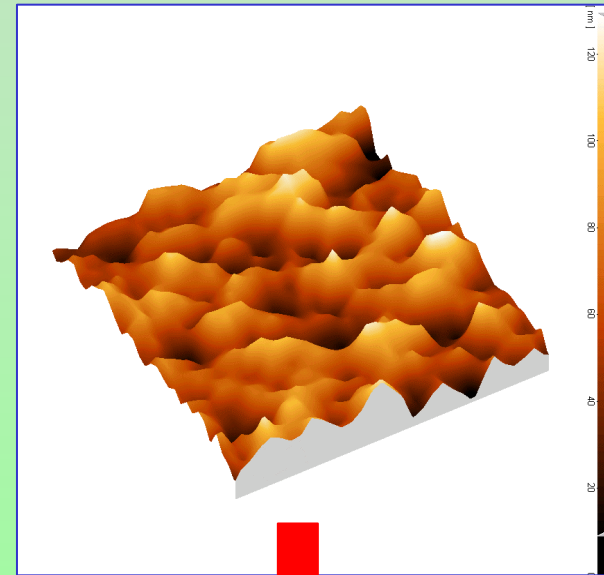
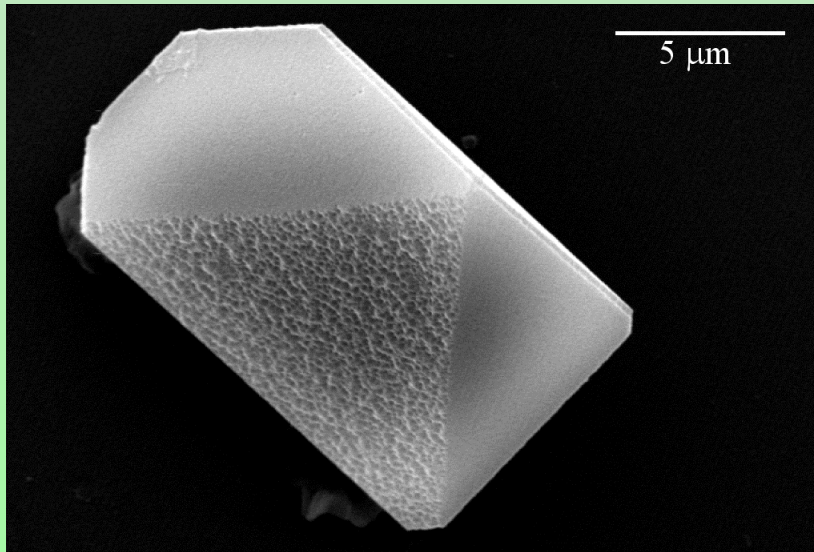
ADSORPTION

Morphodrome showing the change
 $\{100\} \rightarrow \{100\} + \{111\}$
of crystal habit of KCl crystals
with **supersaturation** ($\sigma = \beta - 1$)
and
impurity (Pb^{2+} ion) **concentration**



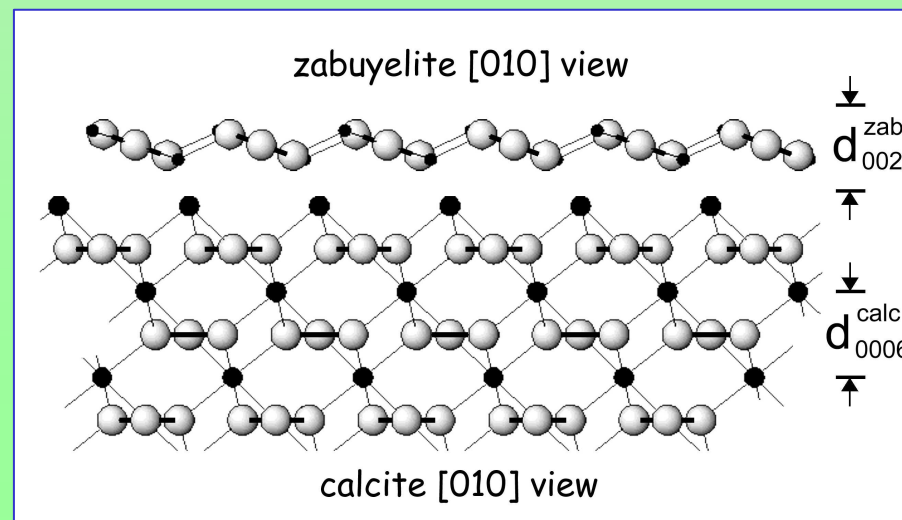
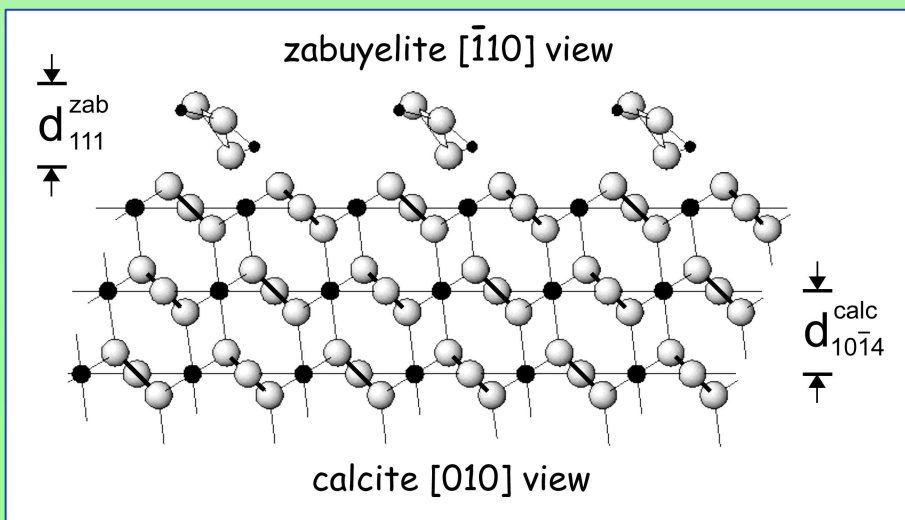
Change of character....

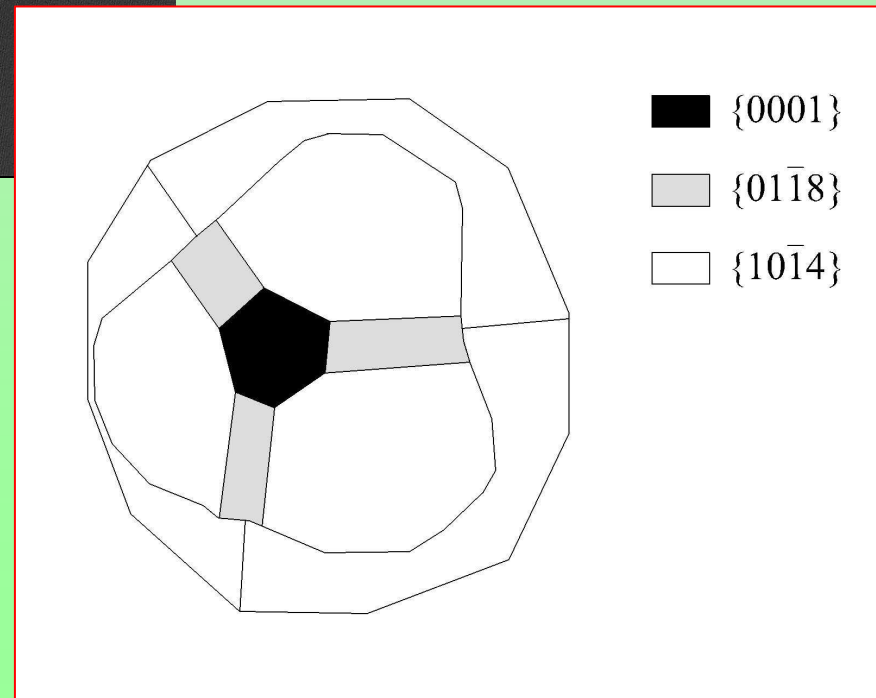
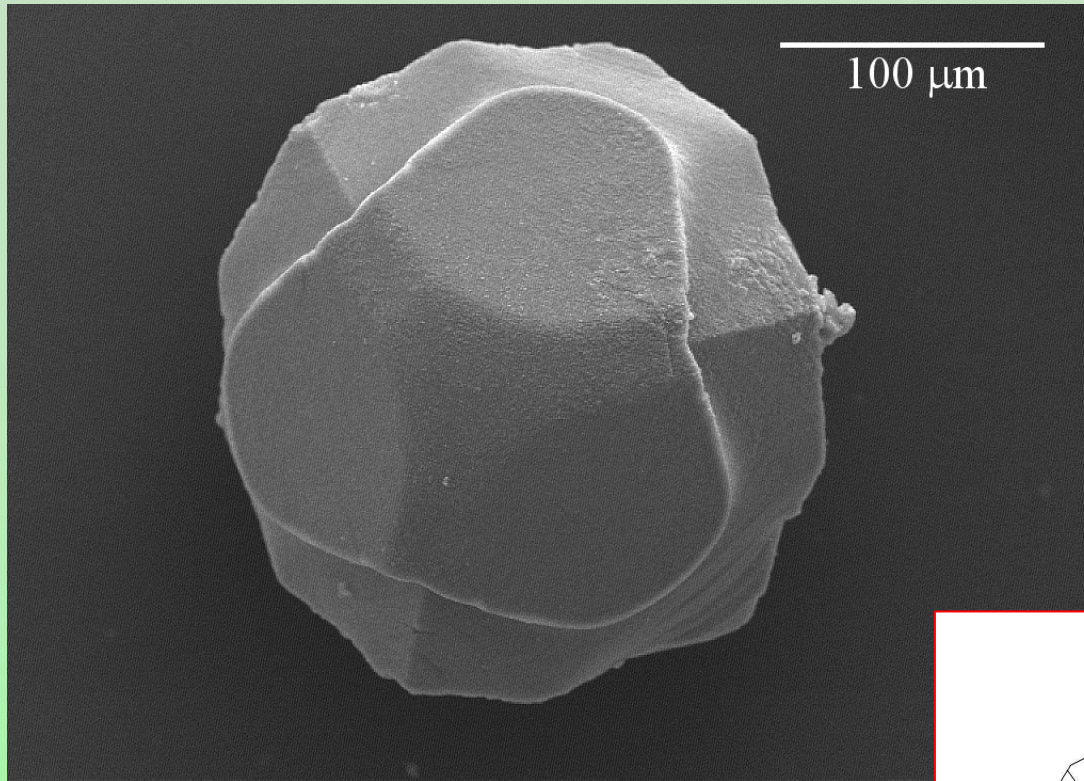
The **{0001}** form of calcite shows a **K character**.
 When growing in pure aqueous solution
 its **surface profile is very rough**, being strongly different from the flat
 one of the adjacent rhombohedron faces.



	Host crystal: calcite form {0001}	Guest crystal: zabuyelite form {001}	Parametric misfit %	obliquity
2D cell vectors and length (nm)	$ [210] = 0.864$ $ [010] = 0.4989$	$ [100] = 0.8359$ $ [010] = 0.4972$	+3.3 +0.34	0°
layer thickness (nm)	$d_{0006} = 0.2843$	$d_{002} = 0.2812$	+ 1.1	

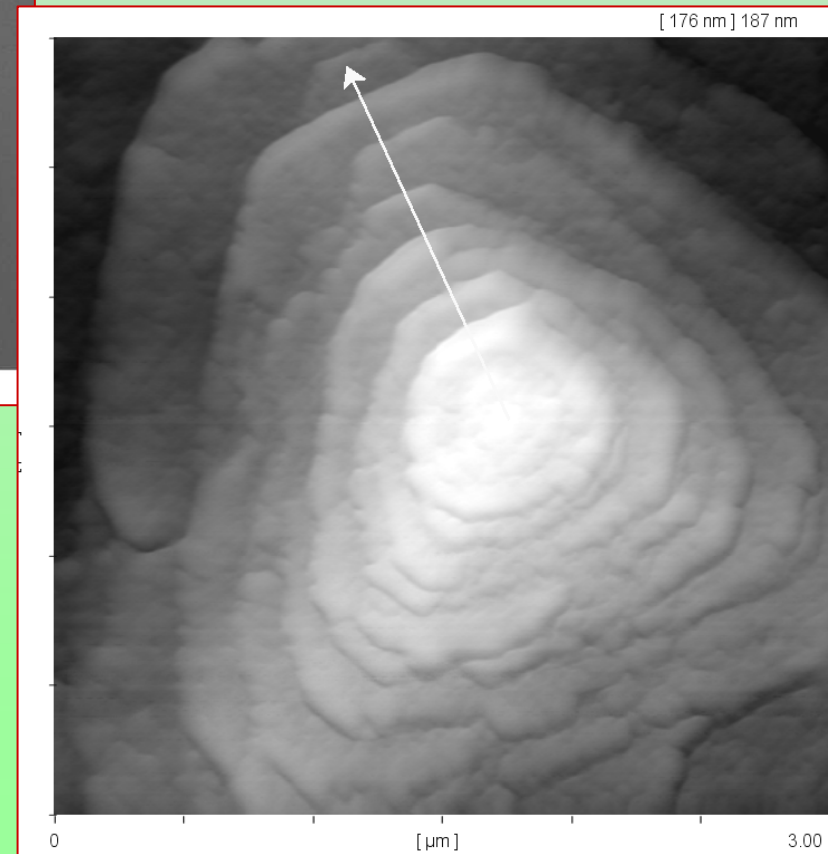
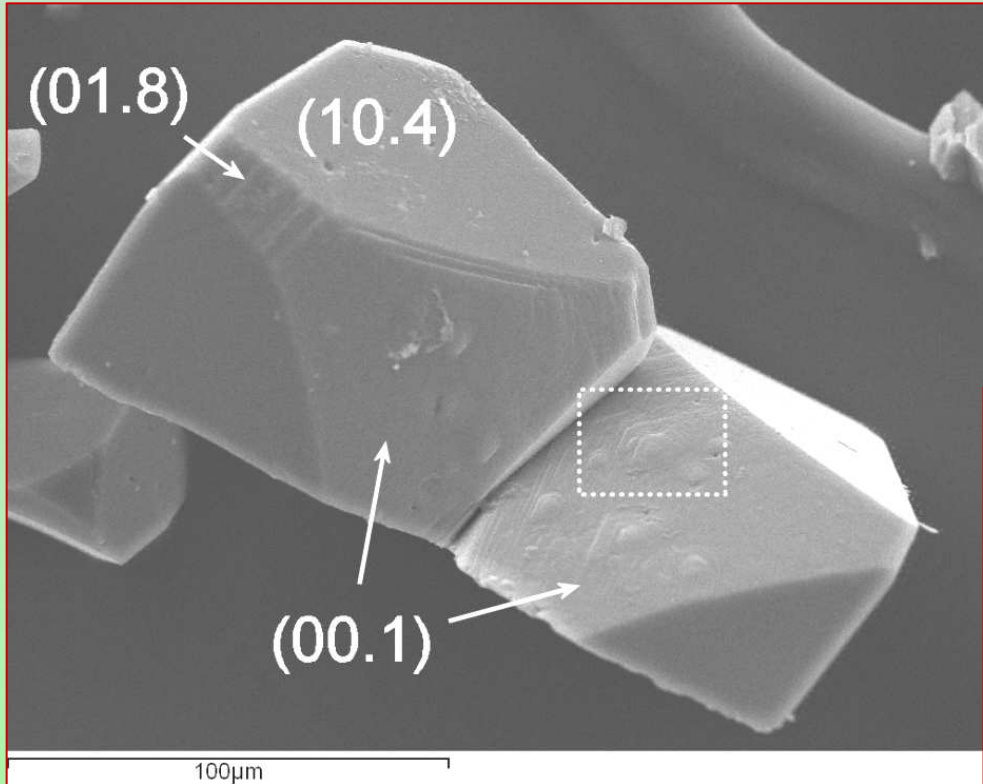
Table 1. **Lattice coincidences** at the {00.1} CaCO₃/ {001} Li₂CO₃ **interface**



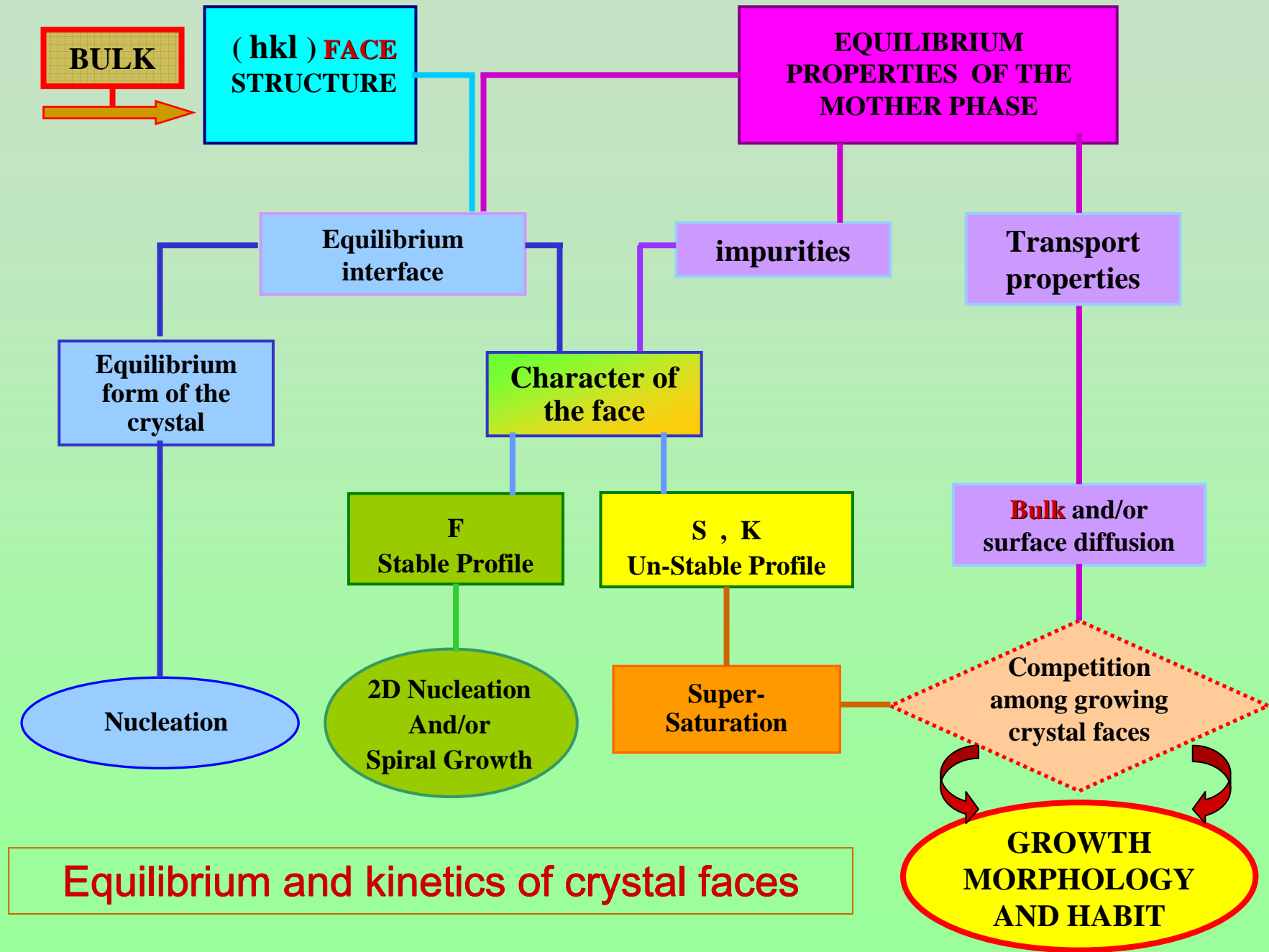


	Calcite {10.4} form	zabuyelite {111} form	misfit %	obliquity
2D cell vectors and length (nm)	$\frac{1}{3} [42-1] = 0.811$ $ [020] = 0.99792$	$ [0-11] = 0.79436$ $ [-110] = 0.97266$	+ 2.09 + 2.6	2.34°
layer thickness (nm)	$d_{10.4} = 0.3043$	$d_{111} = 0.30311$	+ 0.39	

Adsorption through 1D or 2D epitaxies transforms in absorption when the lattice coincidences between host and guest crystals concerns the **thickness of the epitaxial layers** as well



SEM and AFM images show that a kinked face (in pure aqueous solution) transforms in a face growing through layer by layer mechanism in the presence of an impurity



Equilibrium and kinetics of crystal faces

Crystal Growth Group – University of Torino (DSMP)

- Crystallization and morphology (equilibrium and growth) of **Gypsum** from solution, in pure medium and in the presence of copolymers and phosphonates.
- Crystallization of **NaCl, KCl, KI**, from aqueous solution in the presence of **inorganic and organic impurities** (ad-sorption, ab-sorption and 2D epitaxy)
- Nano-cristallization of **Ba, Sr, Ca - carbonates** from solution and gel
- Predicting equilibrium and growth shapes of crystals exhibiting **dipolar surfaces** : NaCl, CaCO₃, ZnO,(ab initio calculation and semi-empirical potentials)