Patterns on the rocks I

Morphology controlled by crystal structure

Juan Manuel García-Ruiz

Laboratorio de Estudios Cristalográficos
Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Granada, España

2013 Santalo's School on the Mathematics of the Planet Earth
Santander, July 15 2013

Patterns on the rocks is a pack of three lectures offering a bunch of problems in mineral pattern formation. From simple shapes controlled by crystal structures to complex shapes mimicking the geometry of life, **Patterns on the rocks** is a pathway across mineral patterns and the current knowledge about their genetic mechanisms.

I. Problems related to formation and shaping of single crystals

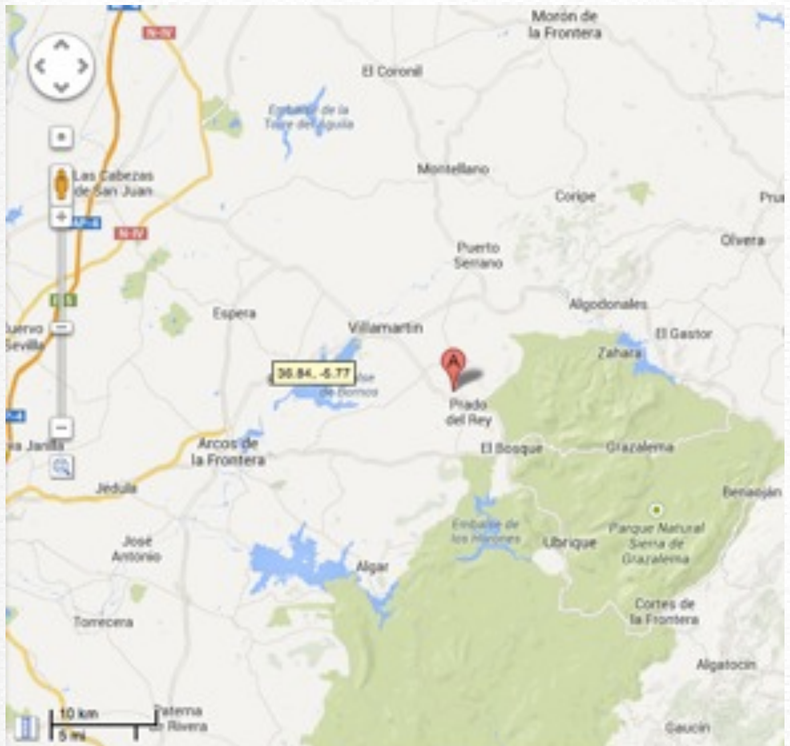
II. Self-organised complex shapes and the problem of life detection

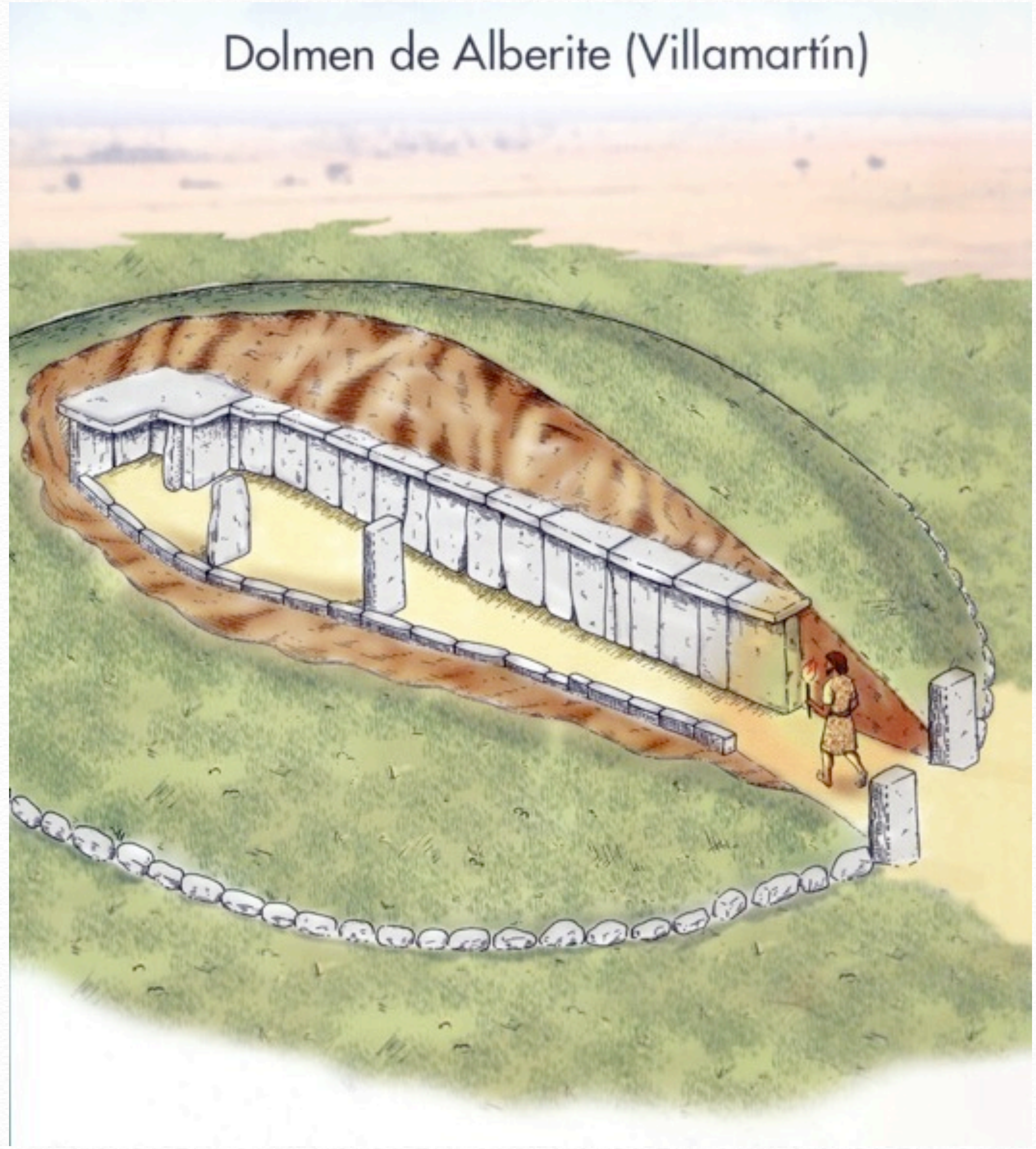
III. Disequilibrium mineral pattern formation

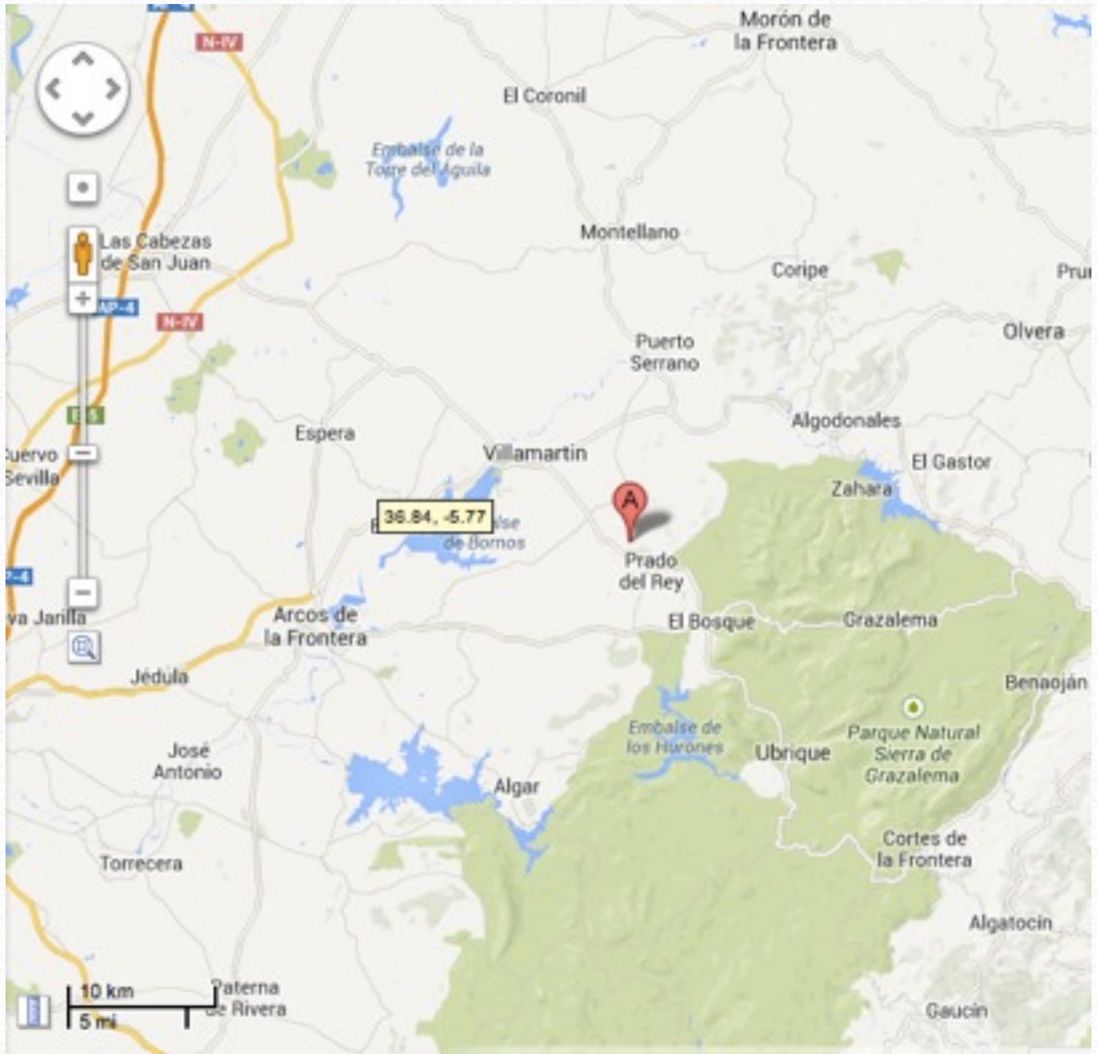
Crystals have fascinated humans since ancient times. May be one of the clearest evidence of such a fascination is the quartz crystal found in a 6000 years-old dolmen in Alberite, Cadiz, South of Spain).

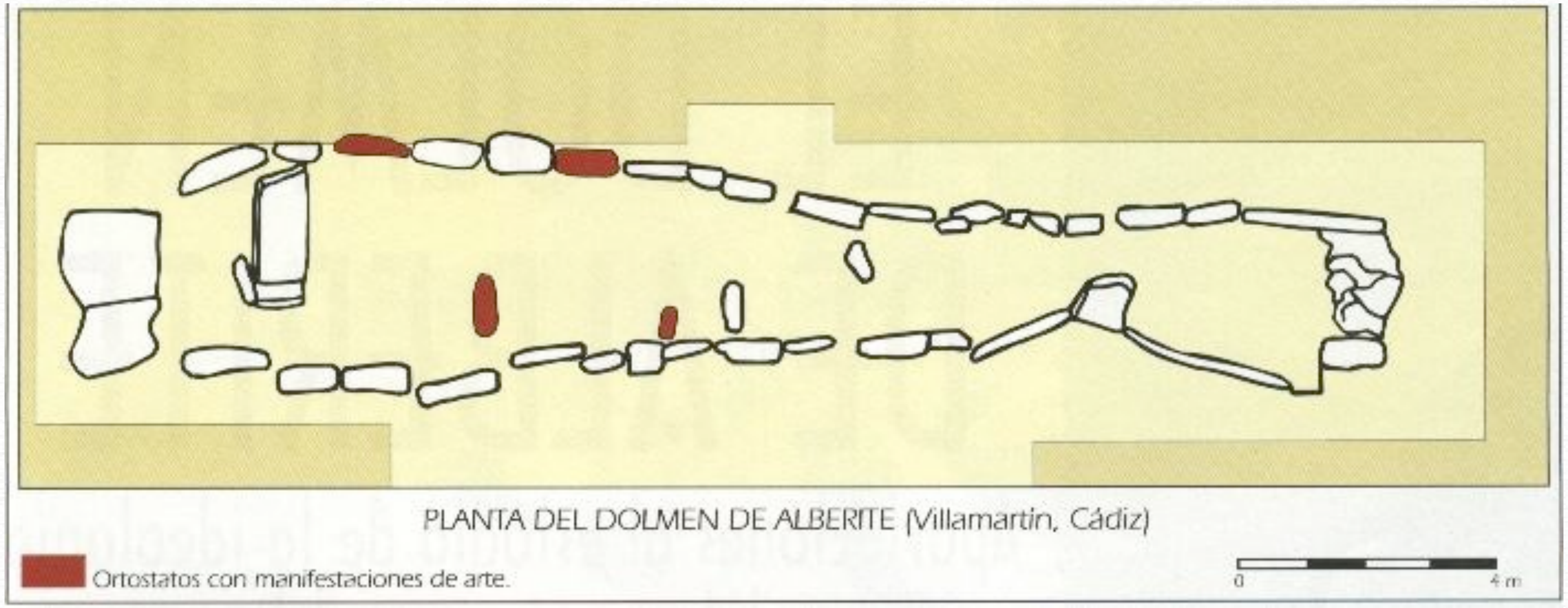
Dolmen de Alberite

Información de José Ramos y Salvador Dominguez-Bella









PLANTA DEL DOLMEN DE ALBERITE (Villamartín, Cádiz)


Ferrol
A Coruña
Santiago de Compostela
Pontevedra
Vigo
Braga
Porto
Lugo
Ourense
Gijón/Xixón
Oviedo
Llanes
León
Santander
Bilbao
Donostia-San Sebastián
Vitoria-Gasteiz
Burgos
Valladolid
Salamanca
Ávila
Madrid
Zaragoza
Lleida
Sabadell
Barcelona
Reus
Andorra
Garrotxa
Toulouse
Agen
Montpellier
Perpignan
Coimbra
Portugal
Lisboa
Setúbal
Badajoz
España
(Spain)
Palancares y Tierra Muerta
València
Albacete
Balearic Sea
Palma
Xàbia
Island
Alacant
Elx
Murcia
Cartagena
Córdoba
Écija
Sevilla
Huelva
Osuna
Granada
Málaga
Costa del Sol
Portimão
Jerez de la Frontera
Gibraltar
Alboran Sea
طنجة
Tanger
وهران
Oran
الجزائر
Alger
البليدة
Blida

Dolmen of Alberite

Smocky quartz crystal found in the funerary site of Alberite, built approximately 6000 years ago.

This pegmatitic quartz crystal does not exist near the area of the location of the Dolmen and therefore has been transported from an area located at least 400 kms away from Alberite.

Why mankind wonders about crystals ?

Shapes drawn by the earth

Water, wind and fire moulded the surface of the Earth over the course of one thousand million years.

The planet on which we all live today was formed around four thousand five hundred million years ago. Way back then, the planet was not only the scene of volcanic activity: the hot earth also began to cool quickly, and condensed water soon began to gather on the surface. And so began the combined action of fire and water. These two forces, along with the wind, carved out the shapes of Earth's inanimate materials, the mineral world. These shapes are the result of the repeated action of simple mechanism which work relentlessly, second by second, constructing an increasingly complex geometry in which curves, and branching are the dominant feature.

Shapes drawn by life

Life helps shape the landscape of by fixing and colouring
the shapes drawn by the water, the wind and the fire

The geological forces which first drew shapes in the Earth's surface were later joined by living organisms, around three thousand million years ago. This new artist became a faithful apprentice in the mineral workshops, copying, retouching here and there, but without changing the style of its master. The geometry of life melted into the geometry of the Earth to form a single landscape of curves and branching: thenatural landscape.

La geometría de la Naturaleza

No hay rectas ni circulos, no hay poliedros.

La geometría de la Naturaleza

No hay rectas ni circulos, no hay poliedros.

Shapes Drawn by Mankind

Less than a couple of millions years ago appeared on the Earth a newly-evolved species. Men drew its own tracks on the Earth's surface

Humans forked off and carved out a straight line in the earth to aerate it and sow seeds, they began to paint the landscape with the arrogance of an apprentice scorning the teachings of his master, with a new pattern which broke away from the landscape style created by Earth and life thousands of millions of years ago.

Shapes Drawn by Mankind

An aesthetic battle began when mankind started to plough the fields with perfectly-straight lines, like in the irrigated fields around Doñana in southwest Spain, where surface water could then flow easily from the well dug out in the sandy soil.

The landscape was retouched, but gently, and this is a minor injury, just like the artificial lagoon that fits delicately into the shallows of the salt marsh in San Fernando, near Cadiz in southern Spain

Shapes Drawn by Mankind

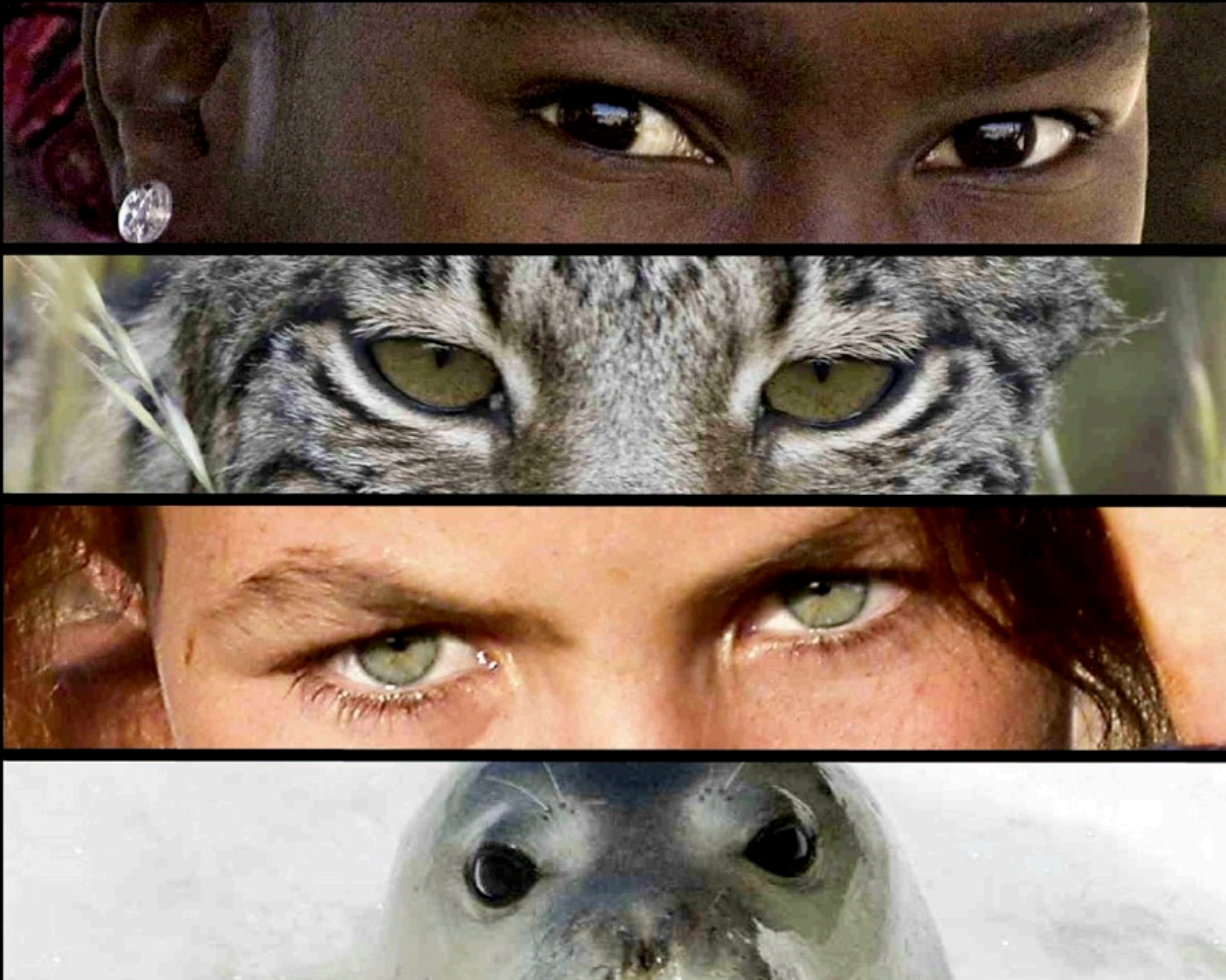
Perhaps more disturbing is the sort of powerful, humiliating grid which erases all trace of natural features, like the one on the salt flats in Sanlúcar de Barrameda, or the vineyards on a dried-out marsh, or the rice plantations on the edge of the Guadalquivir river.

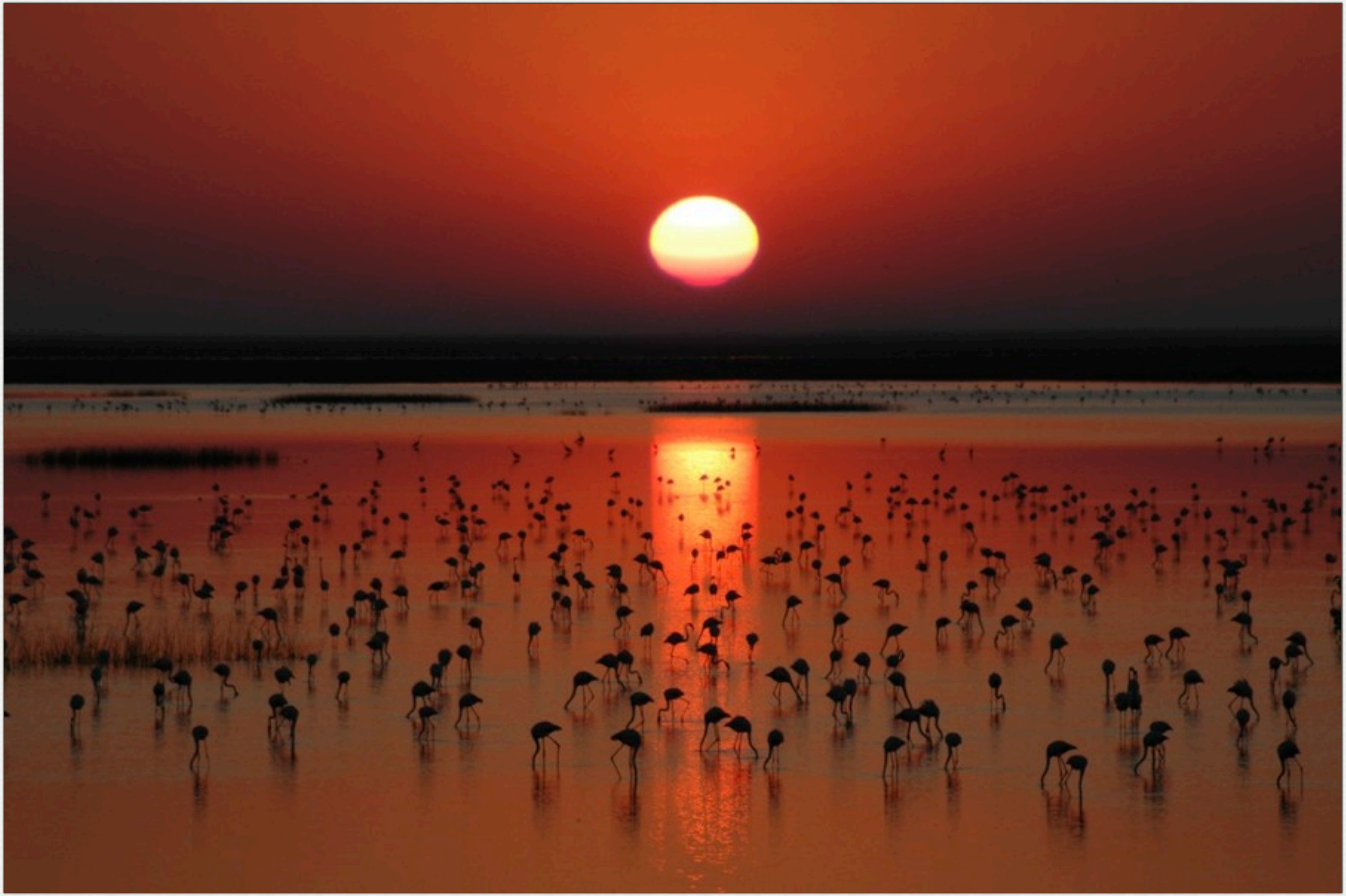
Shapes Drawn by Mankind

As man designs and builds new, increasingly powerful machines, the changes to the landscape are becoming more and more radical, more aggressive, as a result of the overwhelming, cold geometry of urban development which threatens the Earth's natural patterns.

Shapes Drawn by Mankind

The skyline of the large cities is the perfect example of the triumph of the straight line in the urban landscape.





La geometría de la Naturaleza

No straight lines, no circles no

Dolmen of Alberite

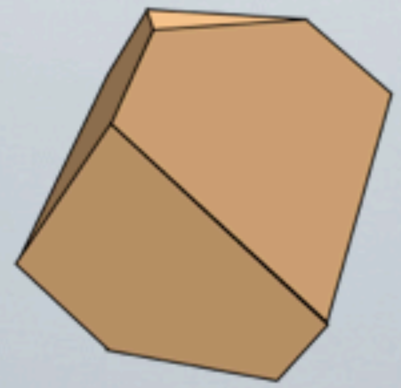
Smocky quartz crystal found in the funerary site of Alberite, built approximately 6000 years ago.

This pegmatitic quartz crystal does not exist near the area of the location of the Dolmen and therefore has been transported from an area located at least 400 kms away from Alberite.

Why mankind wonders about crystals?

Because they were singular natural objects with morphology distinct from other natural objects

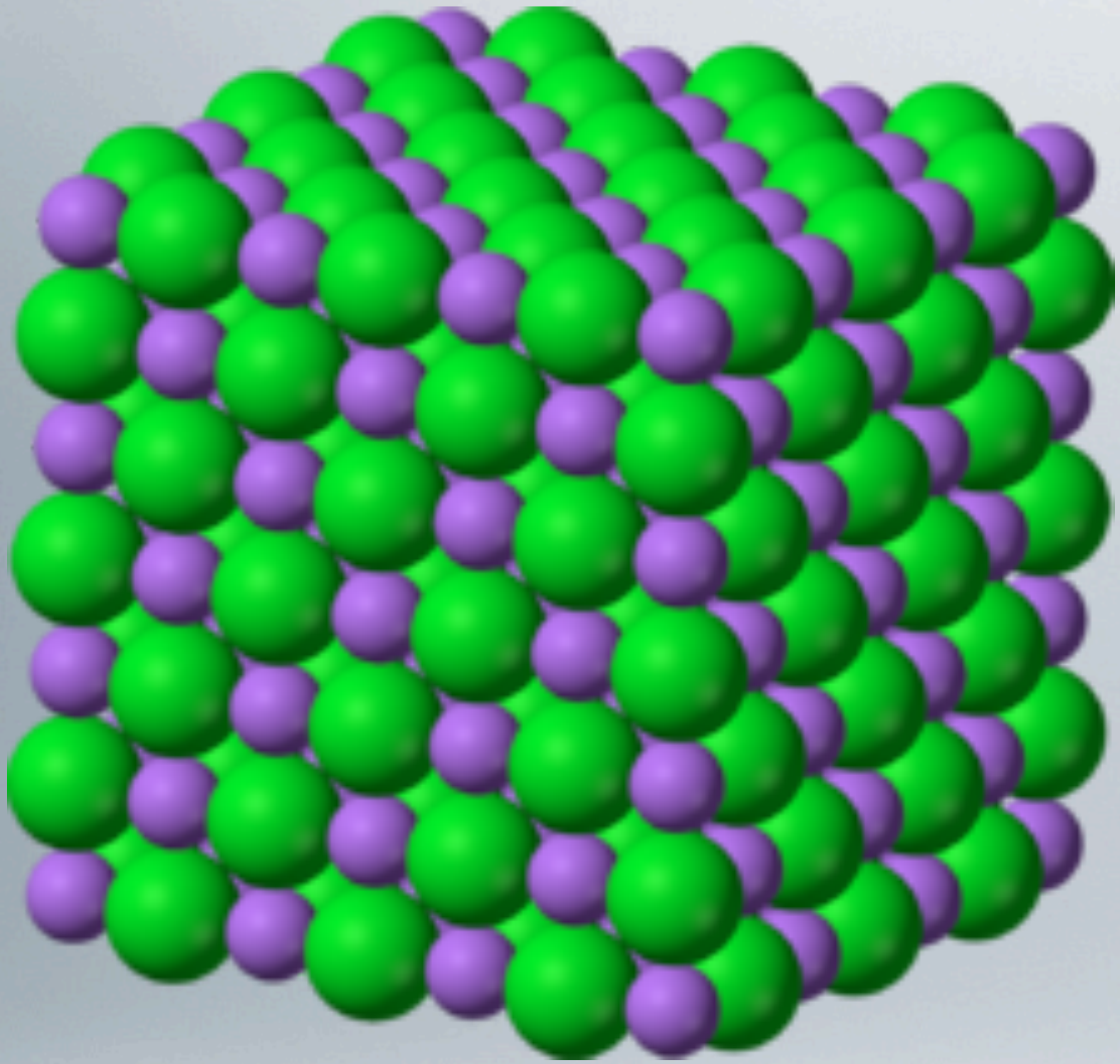
Crystals are shapes of minimal energy



Why are they not spherical, like soap bubbles ?

Melancholia from Durero

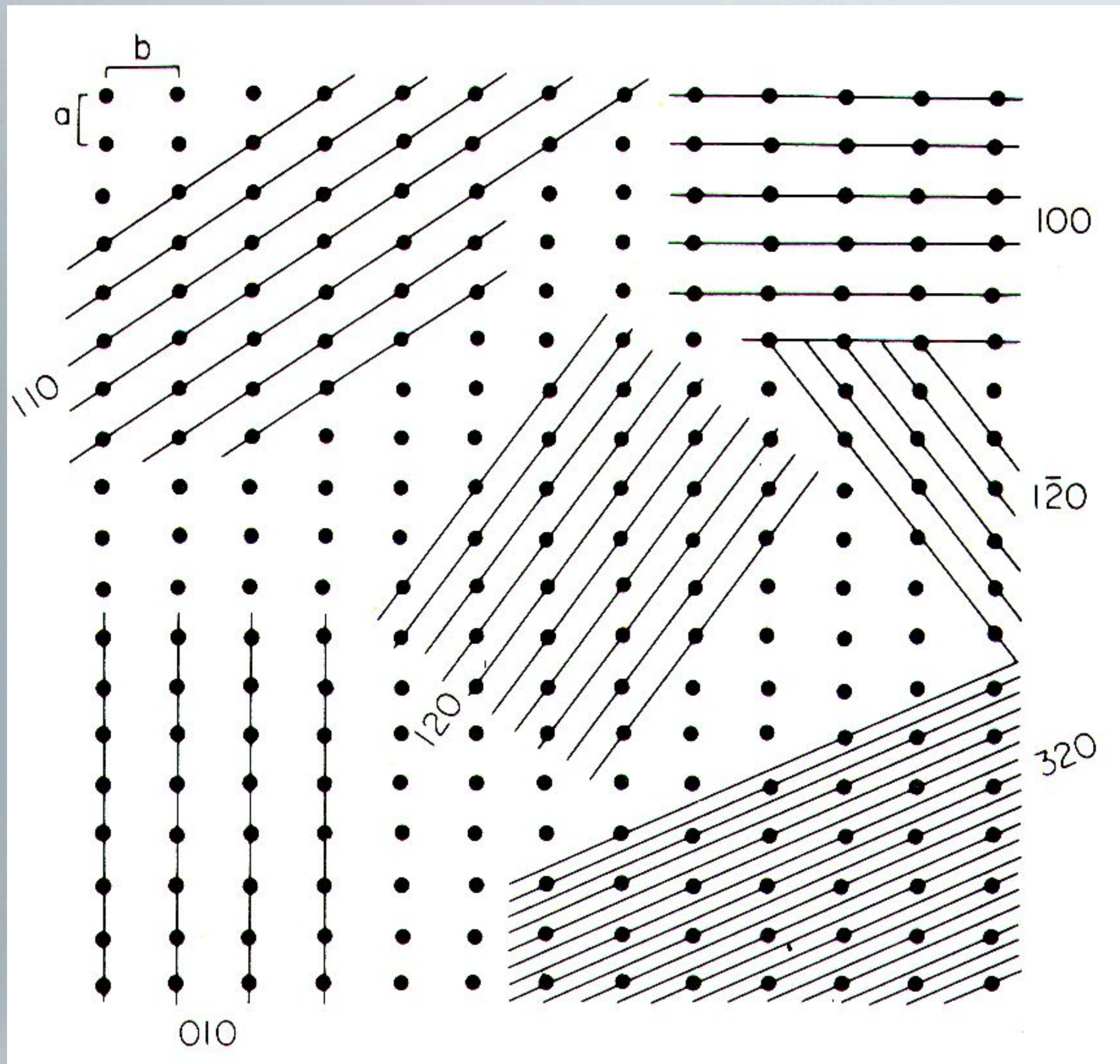
Because crystals are anisotropic 3D structures.



The density and relative strength of bonds in crystals depend on the orientation of the surface. The polyhedral shapes of the crystals result from the anisotropy in specific free-surface energy.

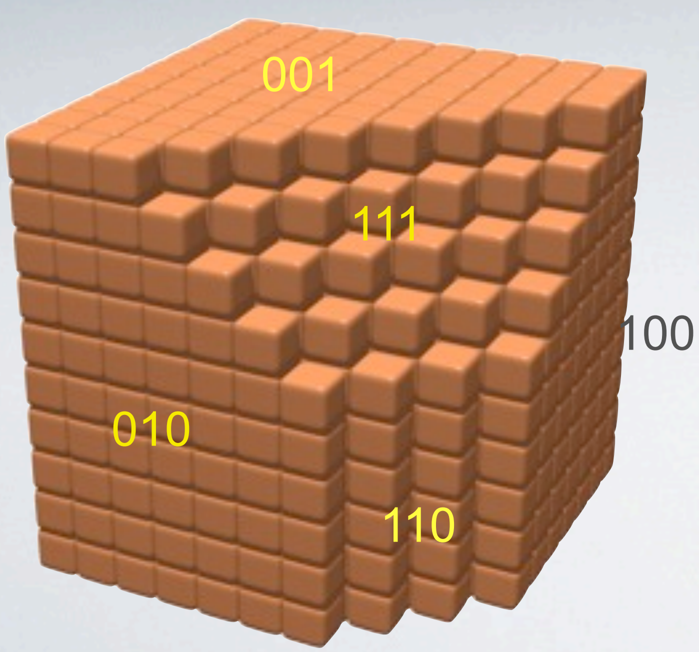
The minimum work required to build a unit interface at a constant volume and temperature in the system is called the specic free-surface energy and denoted gamma

It has units of energy per unit area and is conceptually similar to surface tension, but not identical in the case of solids.



Crystal faces are always parallel to reticular planes.

The higher the reticular density of a family of planes, the larger the interplanar distance

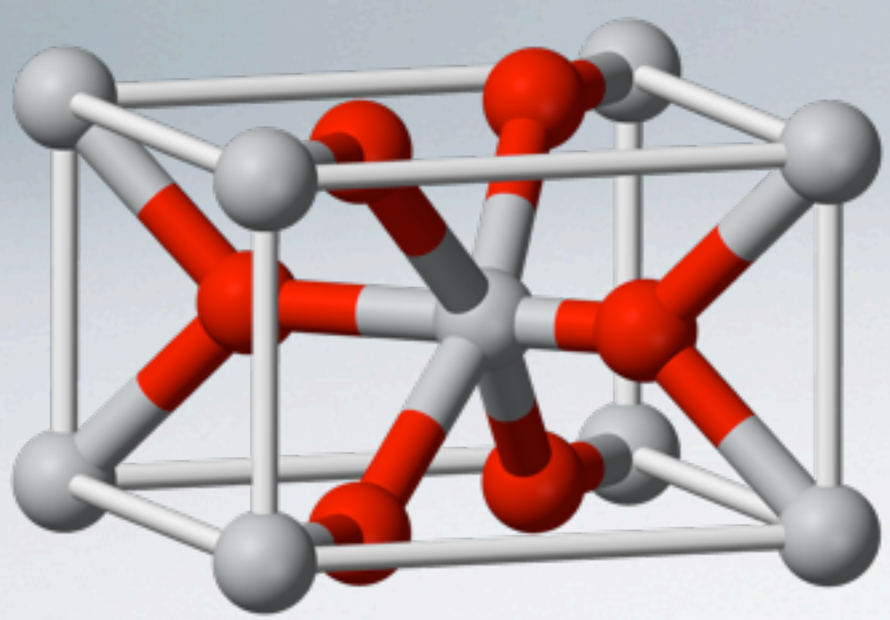


Hartman-Perdok approach

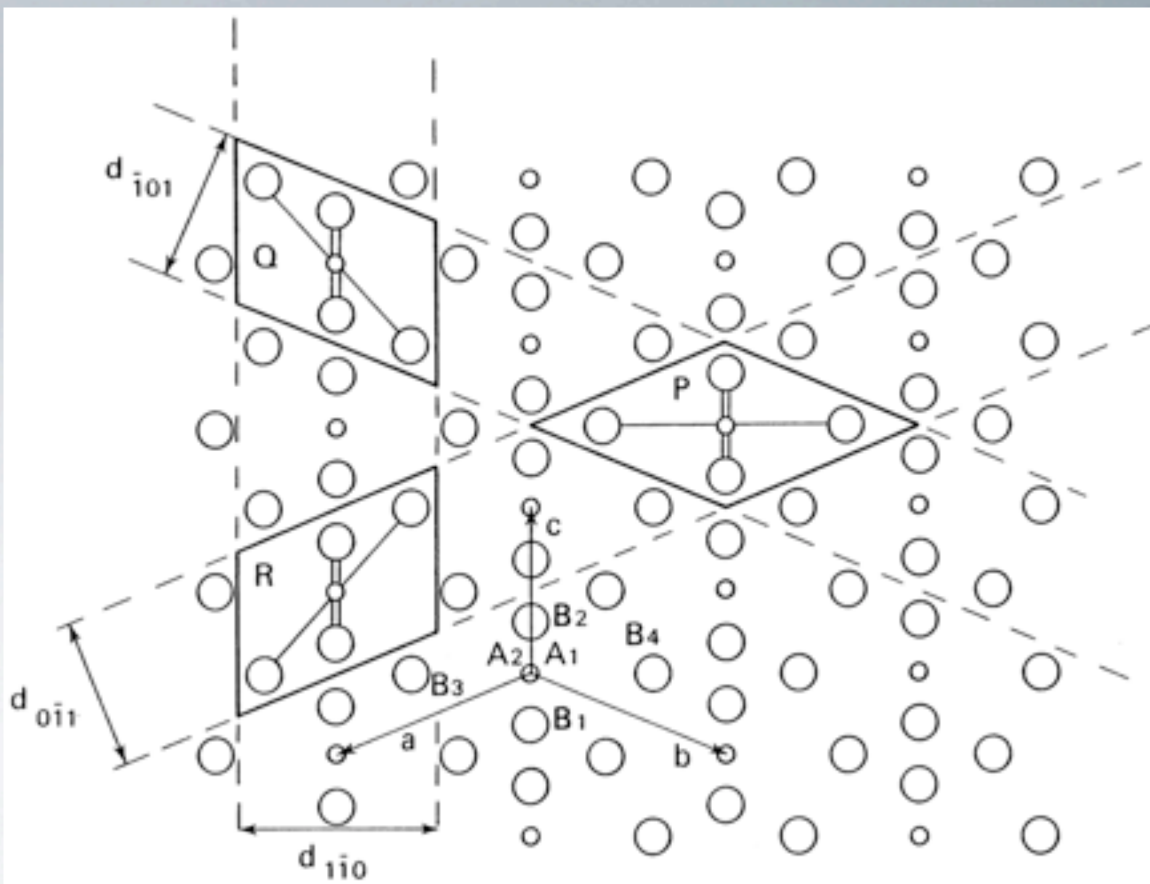
The HP theory is based on the properties of uninterrupted chains of bonds representing strong interactions between growth units. Such a chain is called **Periodic Bond Chain** (PBC) and, in addition,

- PBCs must have an average periodicity [uvw] = ua + vb + wc of the direct primitive lattice (they must be crystallographic directions)

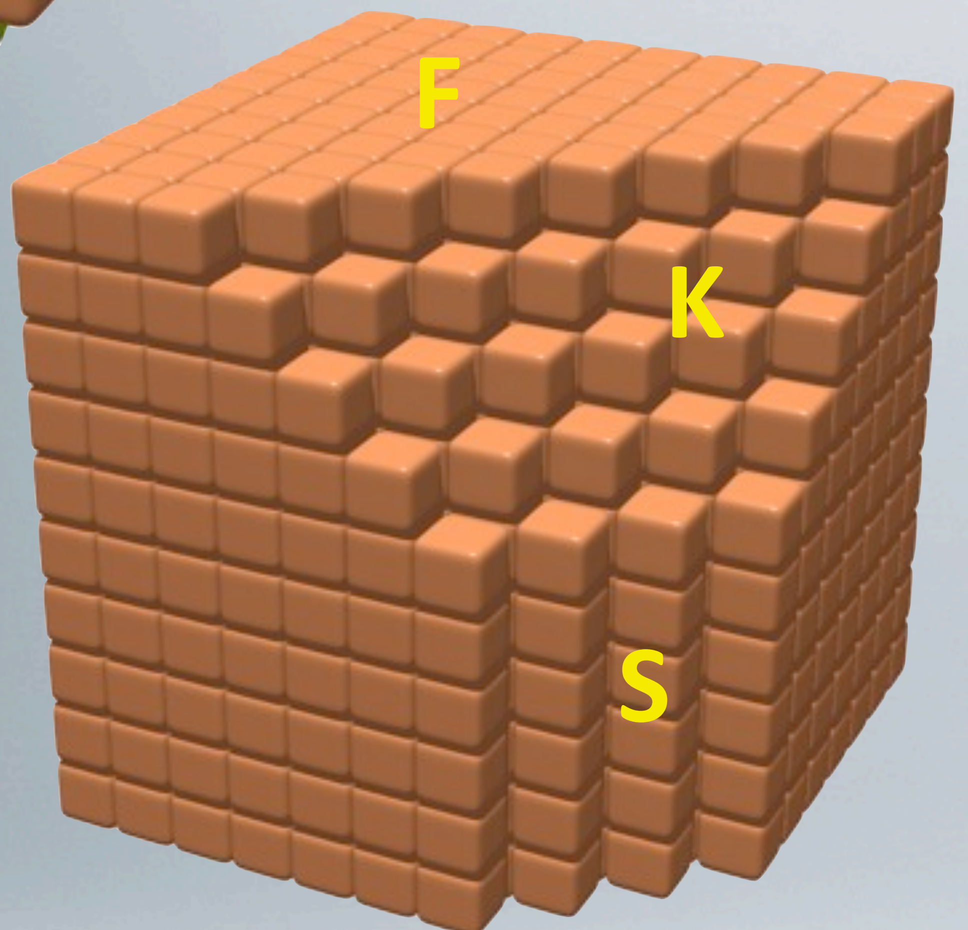
- PBCs must be stoichiometric with regard to the unit cell contents (they are representative of the structure in that direction)



Hartman and Perdock Acta Cryst 8 (1955) 49,



Hartman-Perdok theory



In the classical HP theory, three types of faces are distinguished:

* F-faces parallel to at least two non parallel intersecting PBCs
* S-faces parallel to only one PBC
* K-faces not parallel to any PBC

How do crystals grow?

See: H.V. Alexandru, J Crystal Growth 5 (1969) 115

CRYSTALLIZATION is a phenomenon that consist of two different and consecutive processes.

The first of them is called **NUCLEATION**, which is the result of a phase transition. It deals with the formation of nanoscopic clusters of the new solid phase from the mother solution that may later grow irreversibly to form macroscopic solid crystals.

The second one is the very **CRYSTAL GROWTH** process and it is the subject of the next talk.

THE AIM OF THIS TALK IS TO INTRODUCE YOU TO THE PROBLEM OF NUCLEATION TO HELP YOU TO UNDERSTAND YOUR CRYSTALLIZATION EXPERIMENTS

Reminding simple but important concepts

Solution: An homogeneous phase containing solute and solvent molecules

Equilibrium concentration or solubility (C_e):

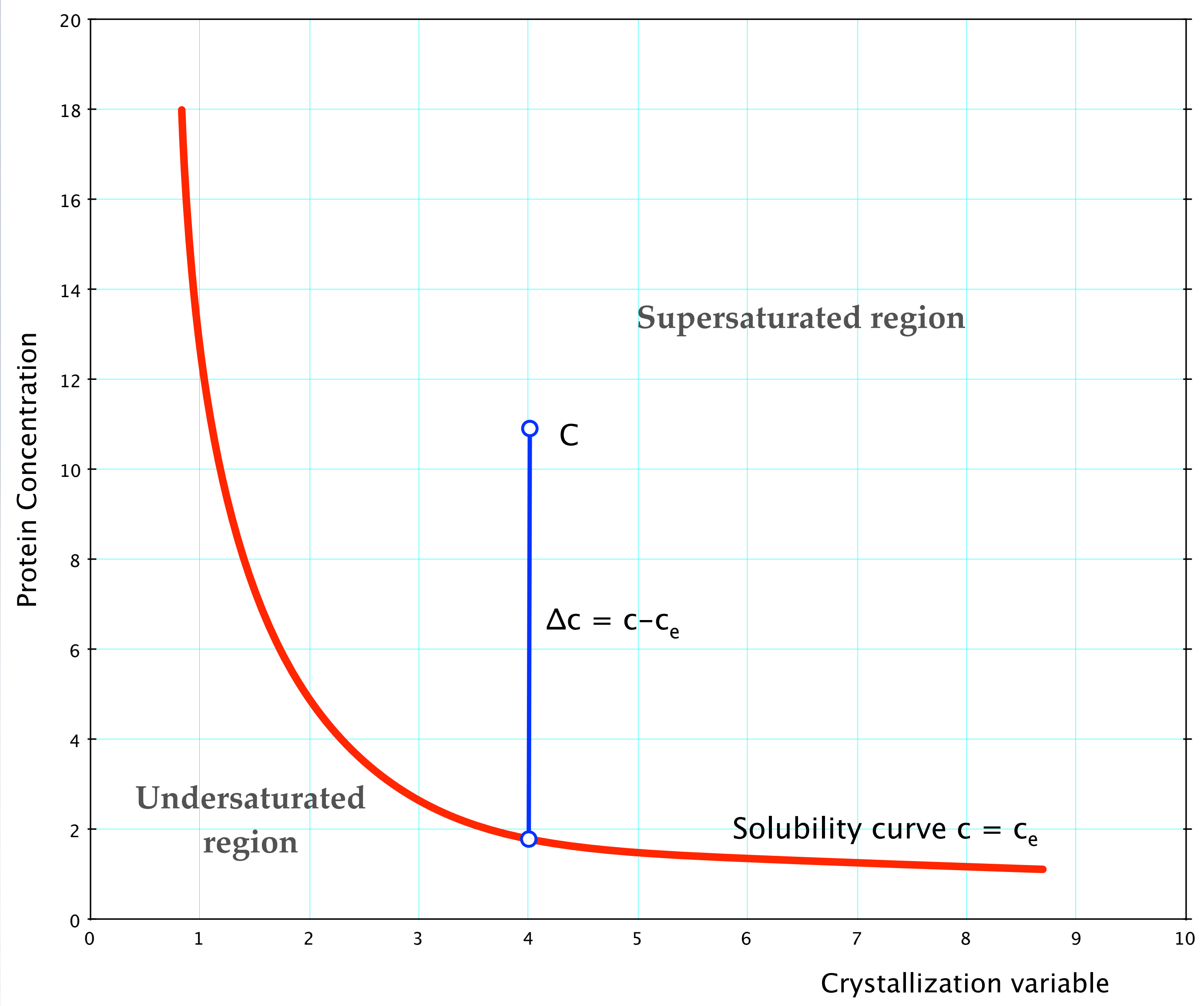
The concentration of solute in solvent at equilibrium with solute crystals, at a given temperature and pH or other variable affecting solubility.

Saturated solution: $C = C_e$

Supersaturated solution : $C > C_e$

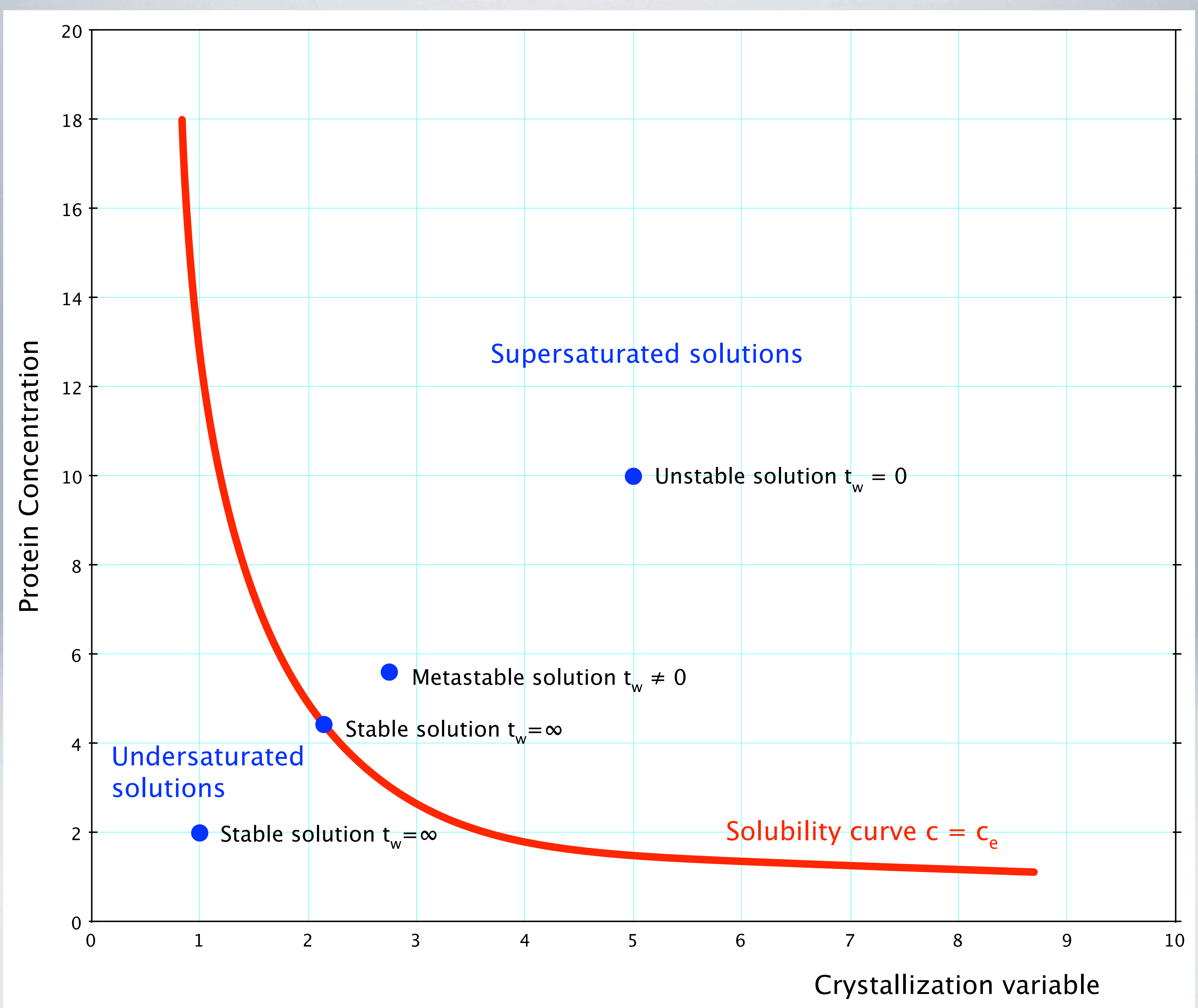
Undersaturated solution: $C < C_e$

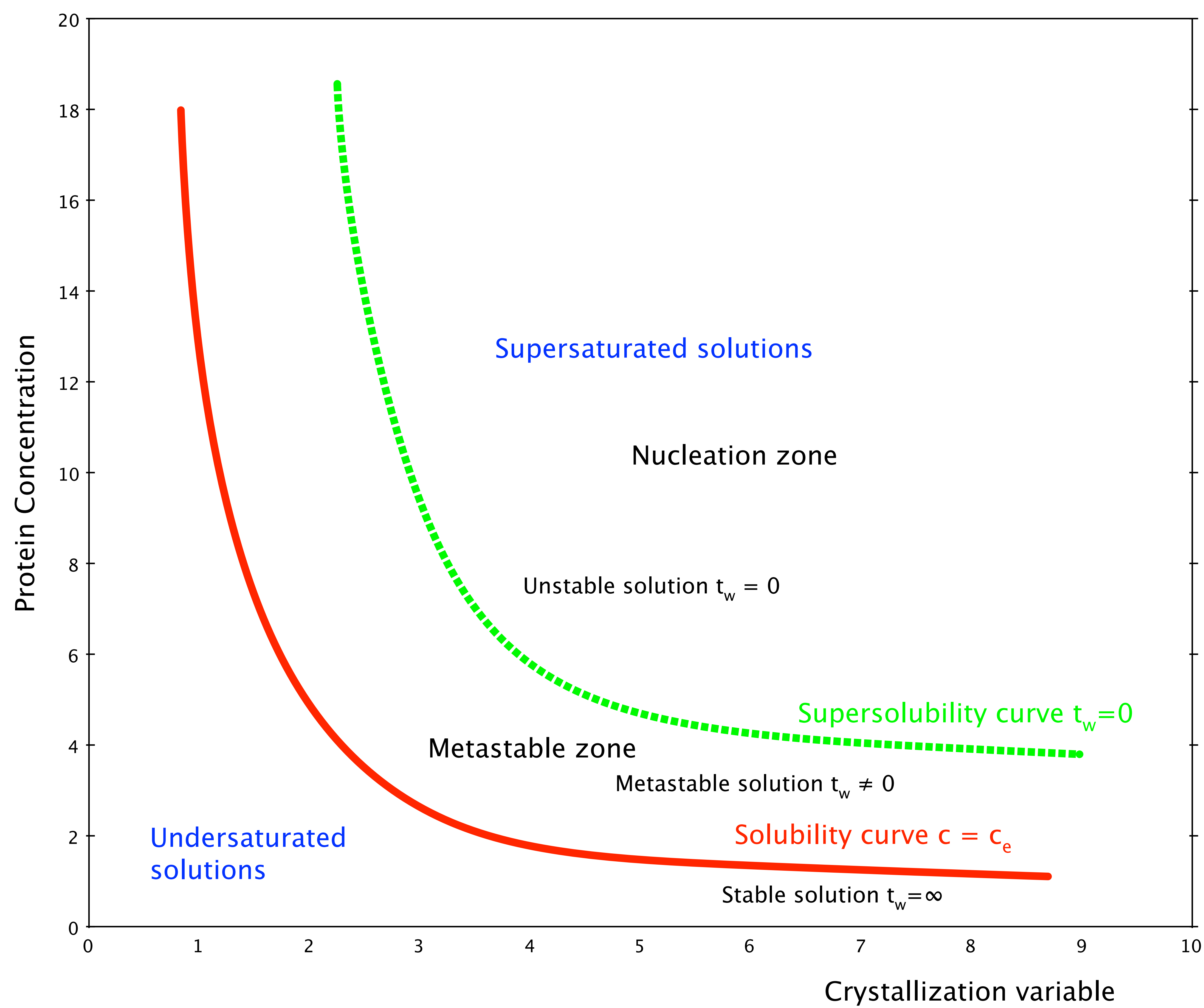
- Undersaturated solution are thermodynamically stable
- Saturated solution are in equilibrium
- Supersaturated solution are thermodynamically unstable



Supersaturation expressions :

- ✓ Supersaturation: $c - c_e$
- ✓ Supersaturation ratio or relative supersaturation: $\frac{c}{c_e}$
- ✓ Absolute supersaturation: $\frac{c - c_e}{c_e}$


Protein Concentration
Crystallization variable
Supersaturated solutions
Unstable solution $t_w = 0$
Metastable solution $t_w \neq 0$
Stable solution $t_w = \infty$
Undersaturated solutions
Stable solution $t_w = \infty$
Solubility curve $c = c_e$
0
2
4
6
8
10
12
14
16
18
20
0
1
2
3
4
5
6
7
8
9
10

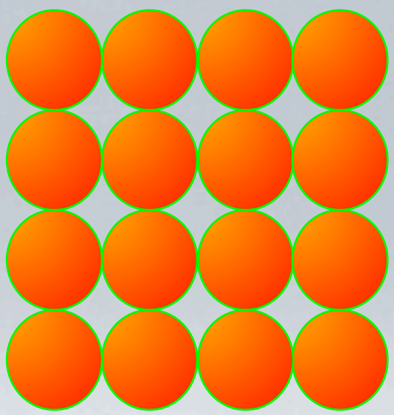

Supersaturated solutions
Nucleation zone
Unstable solution $t_w = 0$
Supersolubility curve $t_w=0$
Metastable zone
Metastable solution $t_w \neq 0$
Solubility curve $c = c_e$
Undersaturated solutions
Stable solution $t_w=\infty$
Protein Concentration
Crystallization variable

An intuitive view of the nucleation process

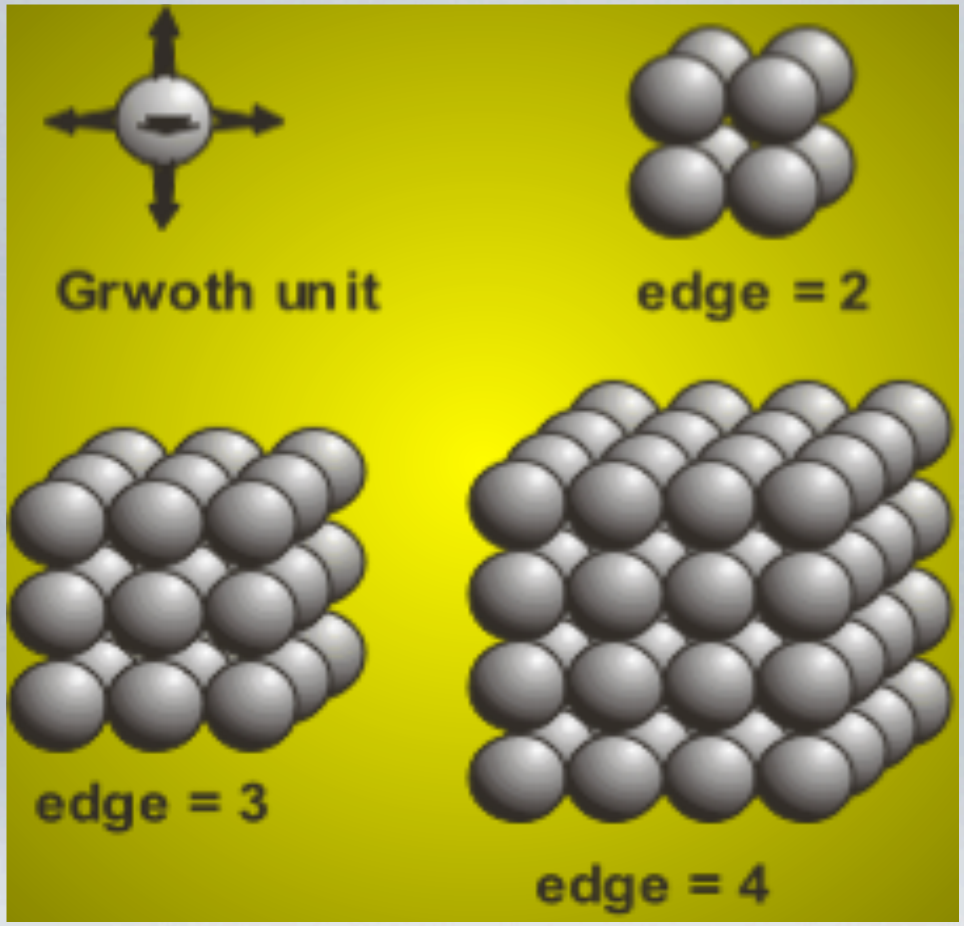
Simulación de nucleación

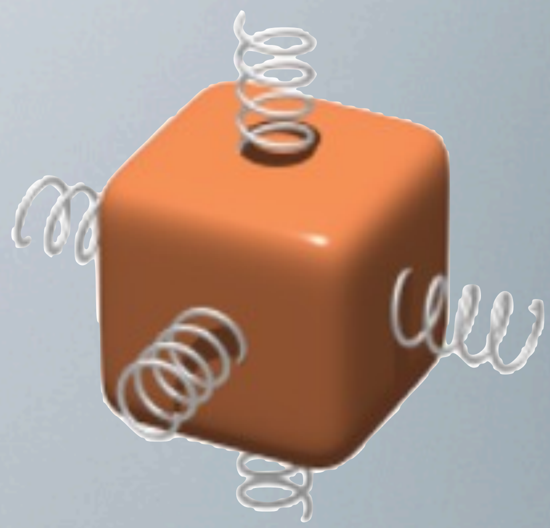
Nucleation

When a cluster form, a surface is created that separates two volumes (the cluster and the mother solution) quite different from a structural viewpoint



The Kossel crystal. The growth unit displays six unsaturated bonds located perpendicular to each face of the cube





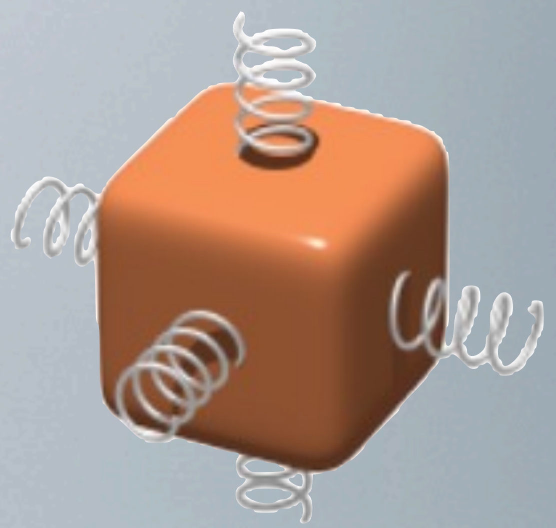
The cohesion of the cluster is proportional to the number de internal saturated bonds versus the number of bonds facing towards the mother solution

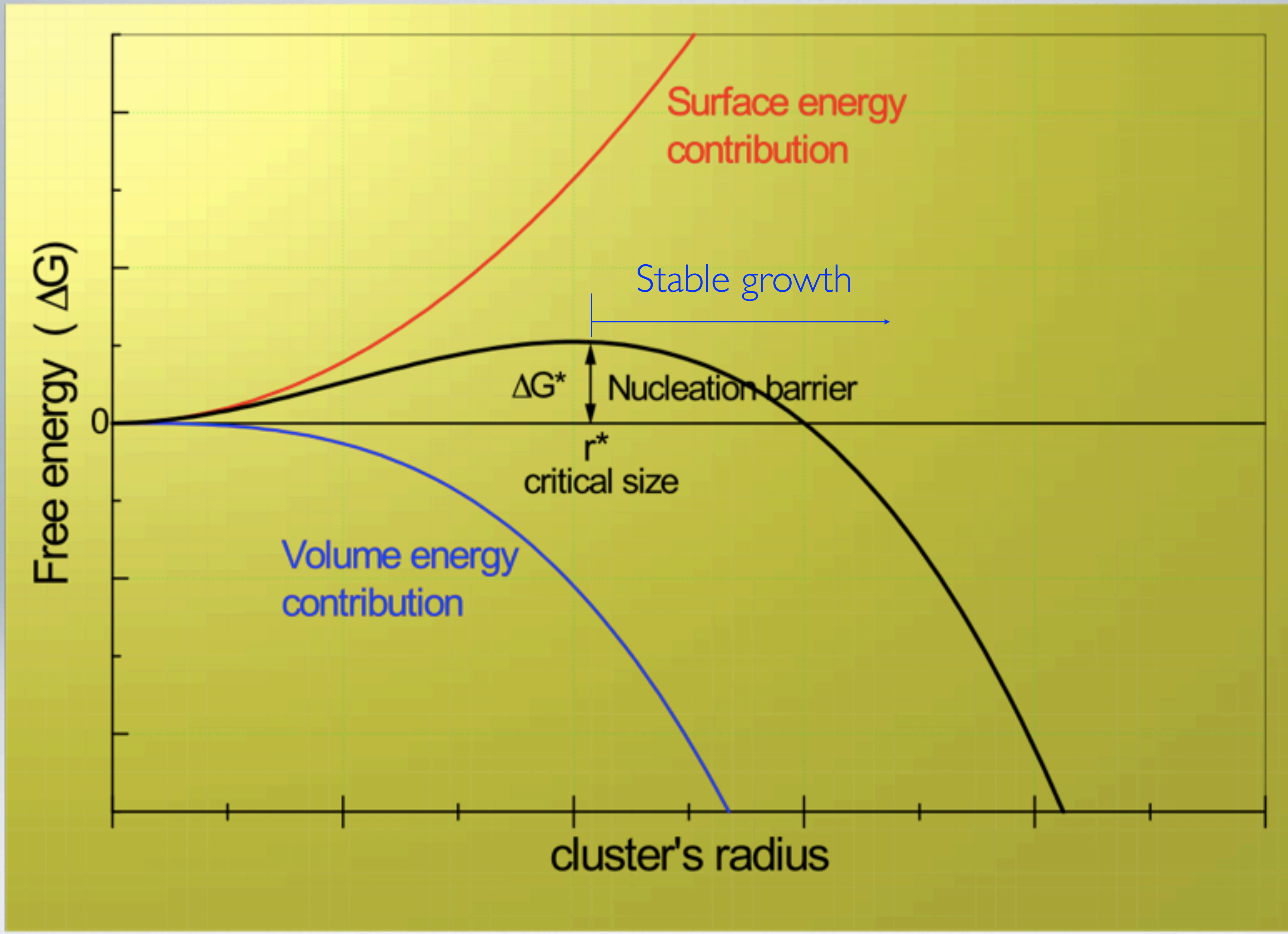
J. M. García-Ruiz, Nucleation of protein crystals, *Journal of Structural Biology*, 142 (2003) 22-31.

Cohesion energy is proportional to the cluster's volume

The surface energy to disagregate is proportional to the cluster's surface

a	$F_S=6*a^2$	$F_A= a^3$
1	6×1^2	$a\ (1)^3$
2	6×2^2	$a\ (2)^3$
3	6×3^2	$a\ (3)^3$
4	6×4^2	$a\ (4)^3$
5	6×5^2	$a\ (5)^3$
6	6×6^2	$a\ (6)^3$
7	6×7^2	$a\ (7)^3$
8	6×8^2	$a\ (8)^3$
9	6×9^2	$a\ (9)^3$




Surface energy
contribution
Stable growth
ΔG*
Nucleation barrier
0
r*
critical size
Free energy (ΔG)
Volume energy
contribution
cluster's radius

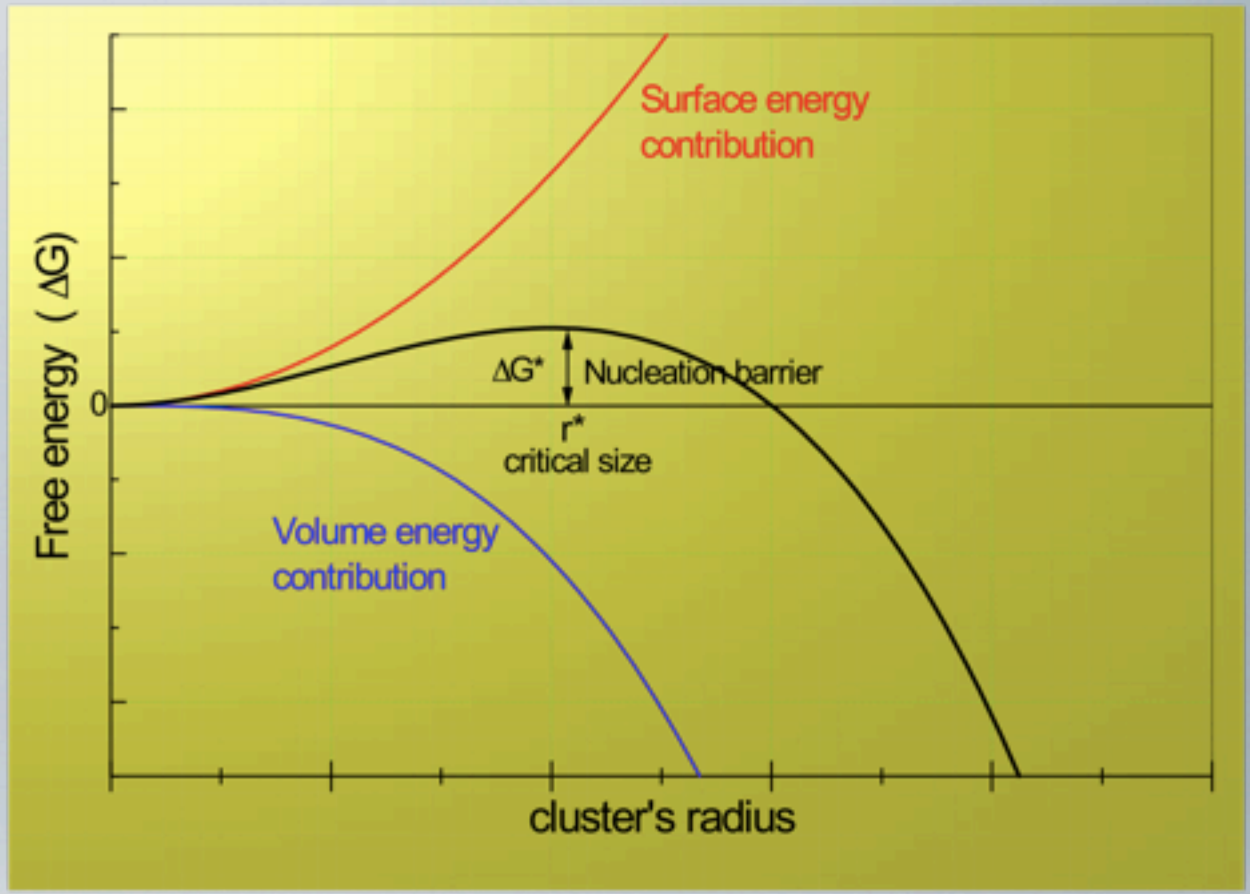
$$\Delta G = \Delta G_v + \Delta G_s = -n(\mu_\alpha - \mu_\beta) + A\gamma$$

$$\mu_\alpha = kT \ln a_\alpha$$
$$\mu_\beta = kT \ln a_\beta$$

$$\mu_\alpha - \mu_\beta = kT \ln S$$

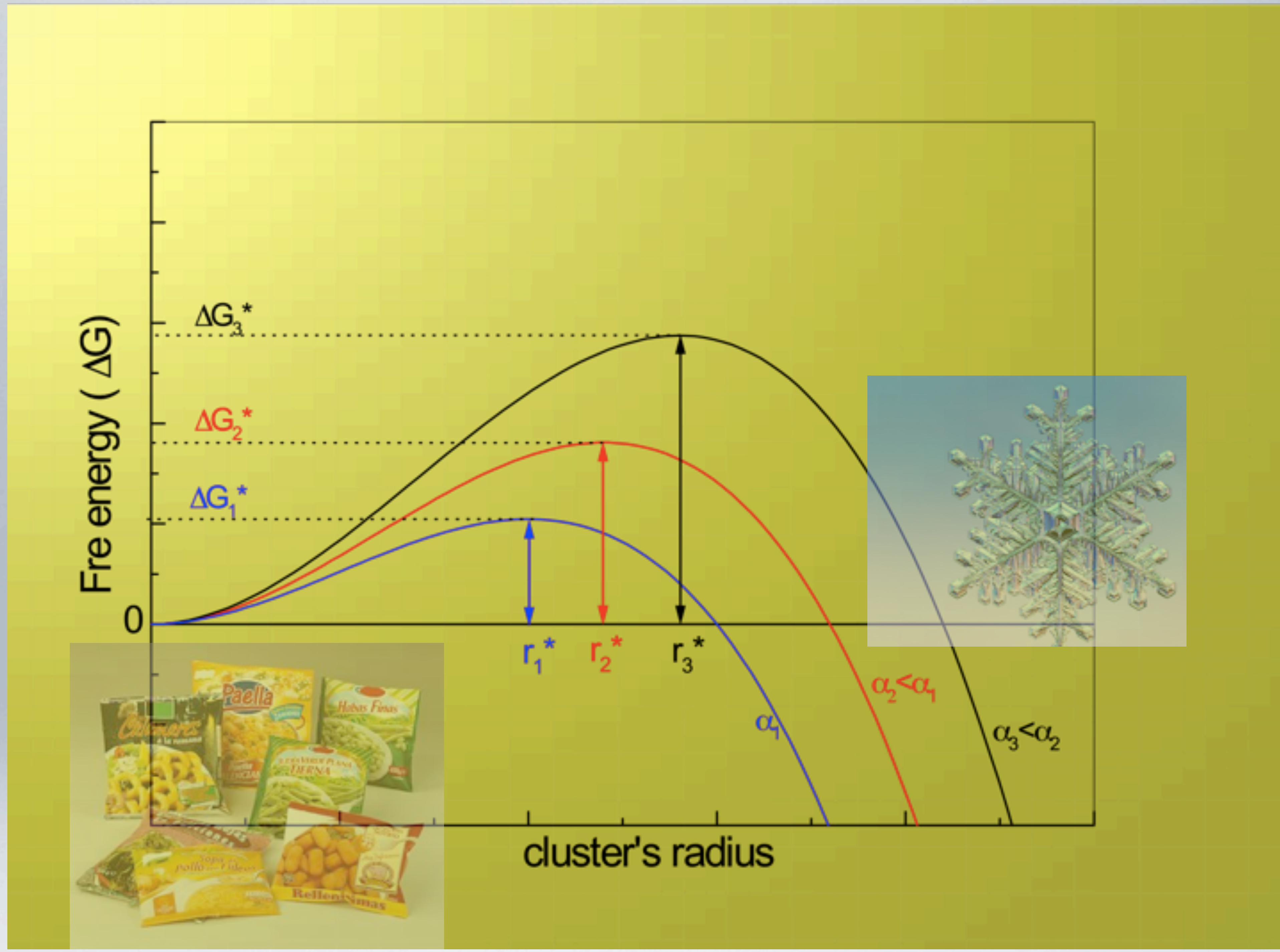
$$\Delta G = -n[kT \ln S] + A\gamma$$

$$\Delta G = -\frac{\frac{4}{3}\pi r^3}{\nu} kT \ln S + 4\pi r^2 \gamma$$



$$r^* = \frac{2\nu\gamma}{kT \ln S}$$

$$\Delta G^* = \frac{16\pi\nu^2\gamma^3}{3[kT \ln S]^2}$$



$$r^* = \frac{2\nu\gamma}{kT \ln S}$$

$$\Delta G^* = \frac{16\pi\nu^2\gamma^3}{3[kT \ln S]^2}$$

According to the Boltzman's law, the probability of a fluctuation of magnitude W is given by : $e^{-\frac{W}{kT}}$. Thus, the probability of a nucleus of size i+1 growth units being created from a cluster of size i is: $e^{\frac{-\Delta G_i}{kT}}$, where ΔG_i is the change of free energy associated to the addition of one growth unit to a cluster of size i. As $n\Delta G_i = \Delta G$, then,

$$\frac{N_n}{N_1} = \exp\left(\frac{-\Delta G}{kT}\right)$$

The nucleation frequency J, i.e. The number of nuclei per unit of volume and unit of time that achieve the critical size can be expressed as:

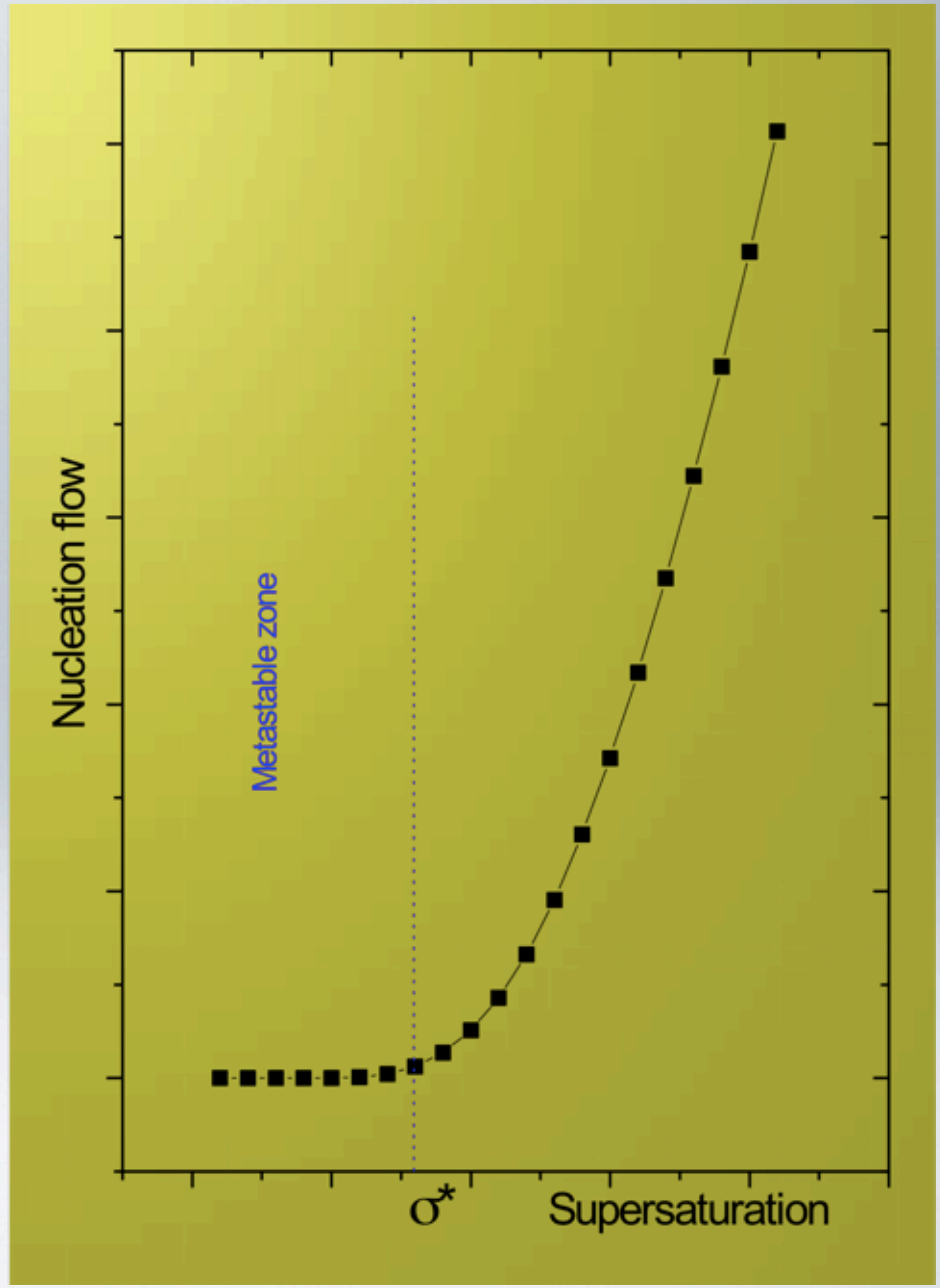
$$J = \kappa_0 \exp\left(\frac{-\Delta G^*}{kT}\right)$$

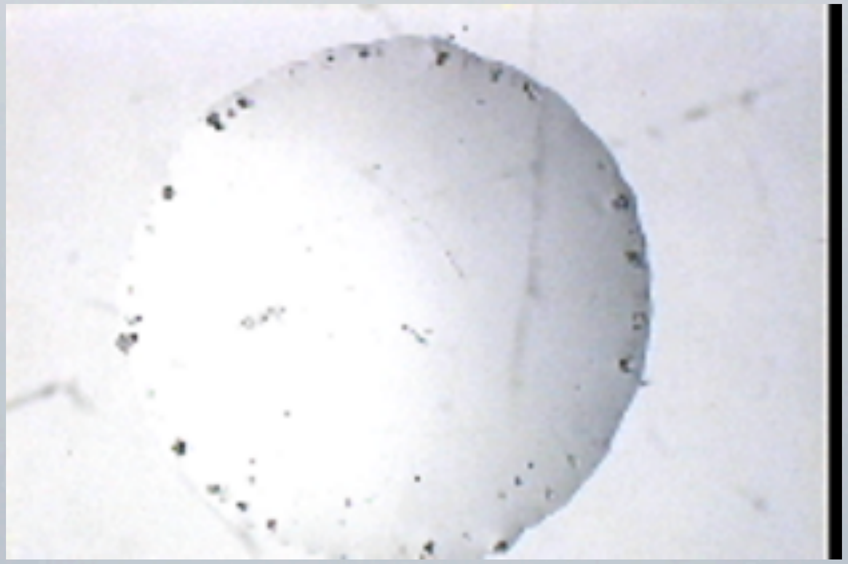
Substituying the value of ΔG^* in the last equation we got:

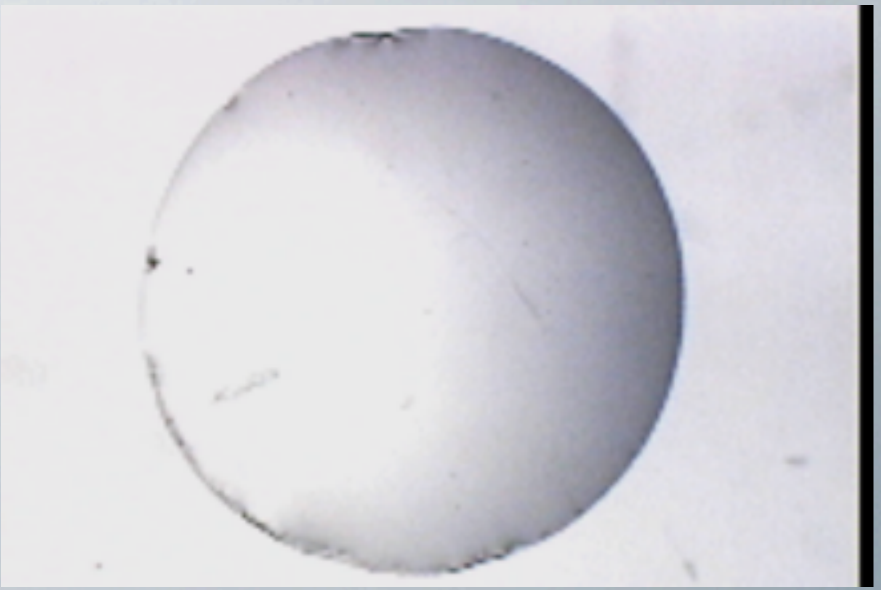
$$J = \kappa_0 \exp\left(-\frac{16\pi\upsilon^2\gamma^3}{3(kT)^3[\ln S]^2}\right)$$

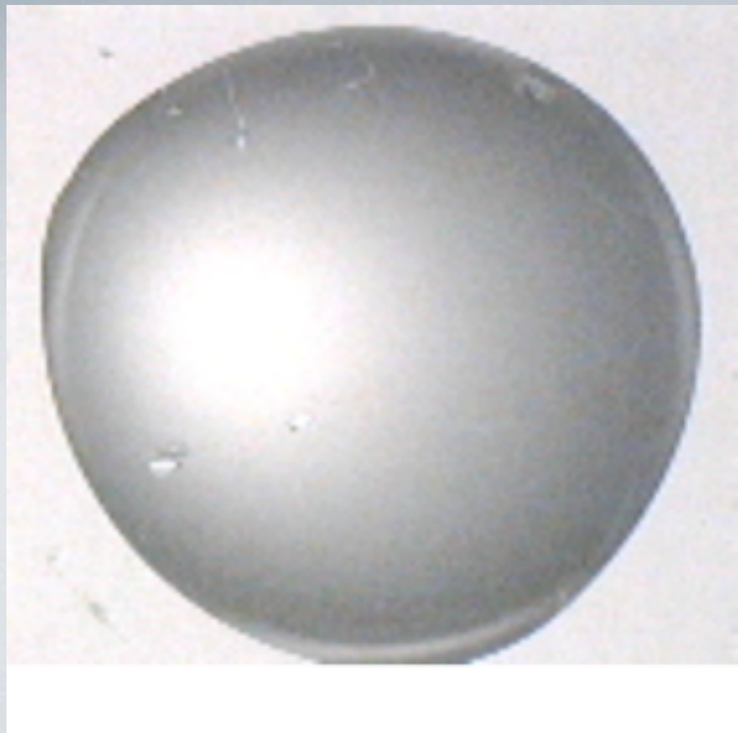
Nucleation frequency J is defined as the number of stable nuclei forming per unit of time and unit of volumen. It is given by:

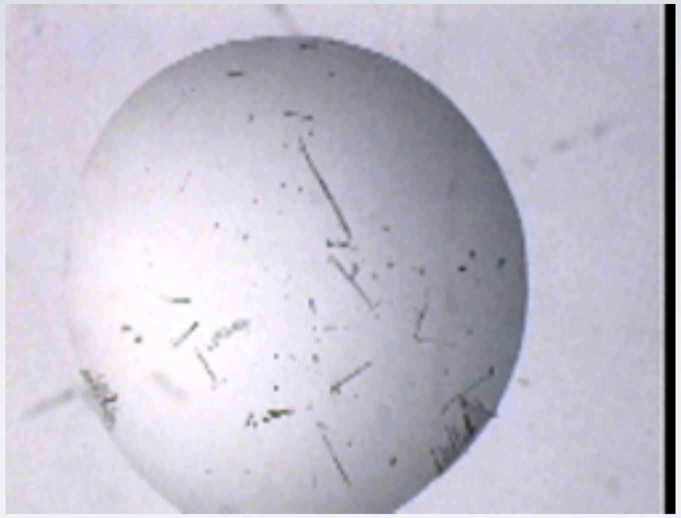
$$J = \kappa_0 \exp\left(- \frac{16\pi\upsilon^2\gamma^3}{3(kT)^3[\ln S]^2} \right)$$

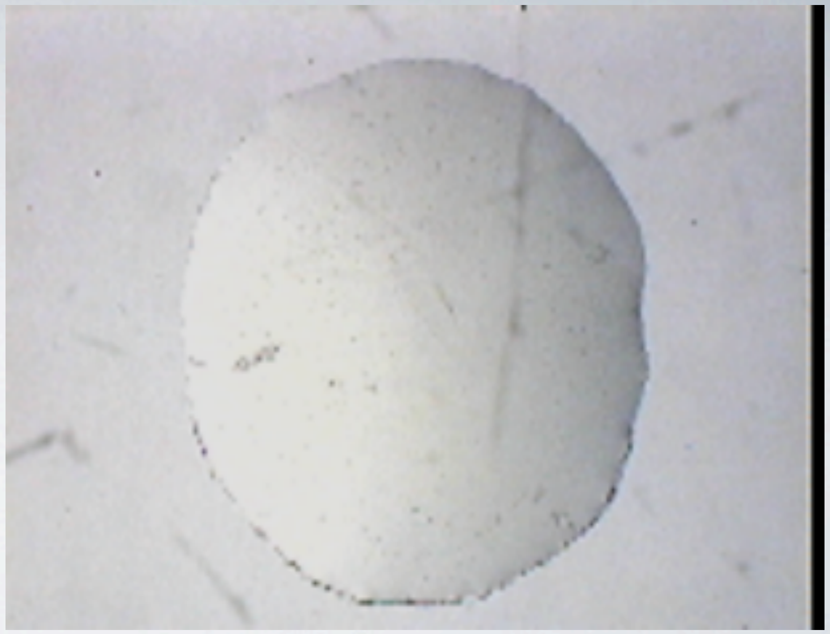












Polimorphism

Compounds that are able to adopt different structural configurations

Diamond	Graphite
cubic carbon	hexagonal carbon


BPTI-NaBr Phase Transition J.P. Astier and S. Veesler CINaM-CNRS, Marseille, France

Ostwald phenomenological rule

The metastable phase form first and then it transform to the more stable one

Vaterite, aragonite calcite

Polymoprhs of calcium carbonate

The case of calcium sulphate precipitation

The calcium sulphates

Gypsum: $CaSO_4 \cdot 2\,H_2O$

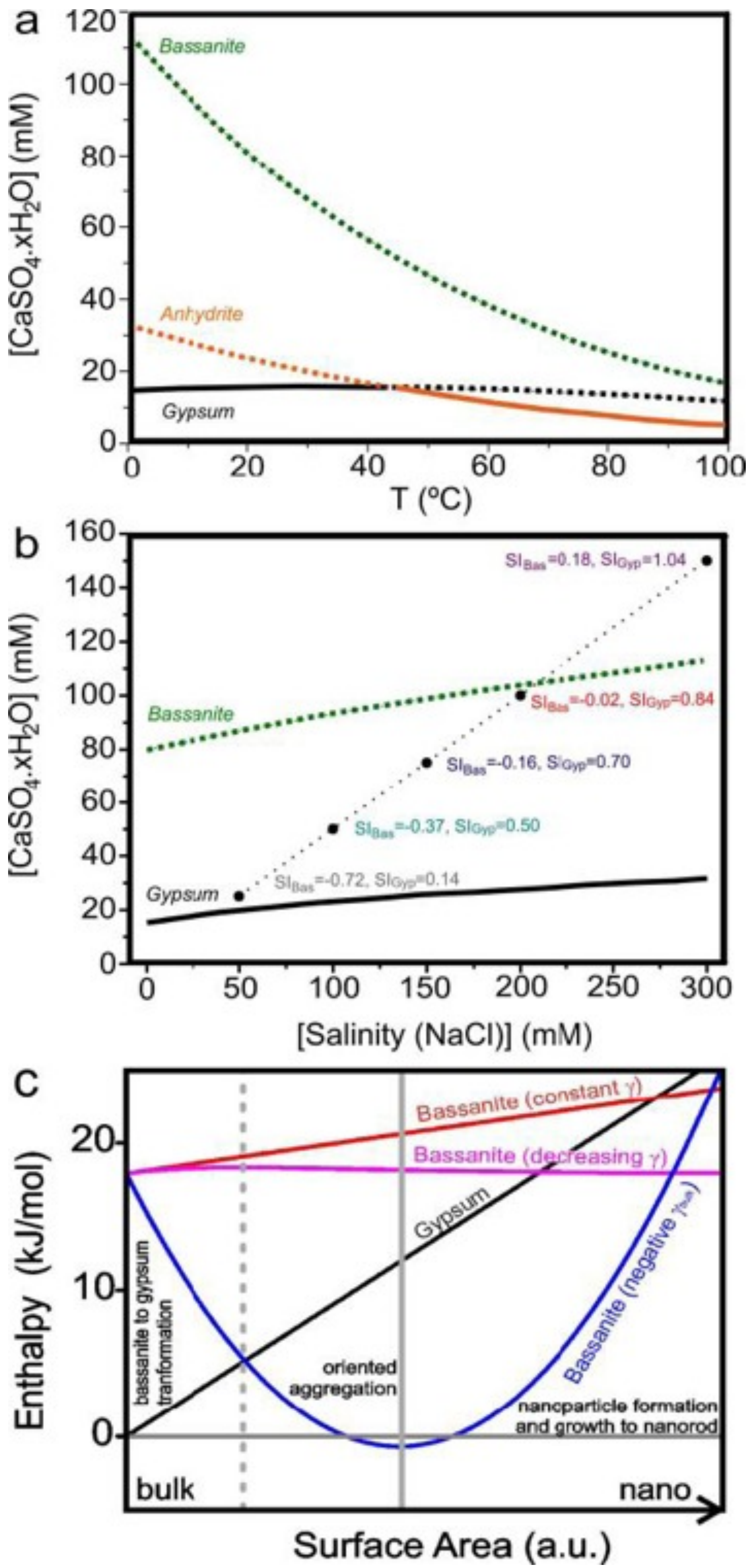
Monoclinic
Point symmetry group (2/m)
Space symmetry group: A2/a

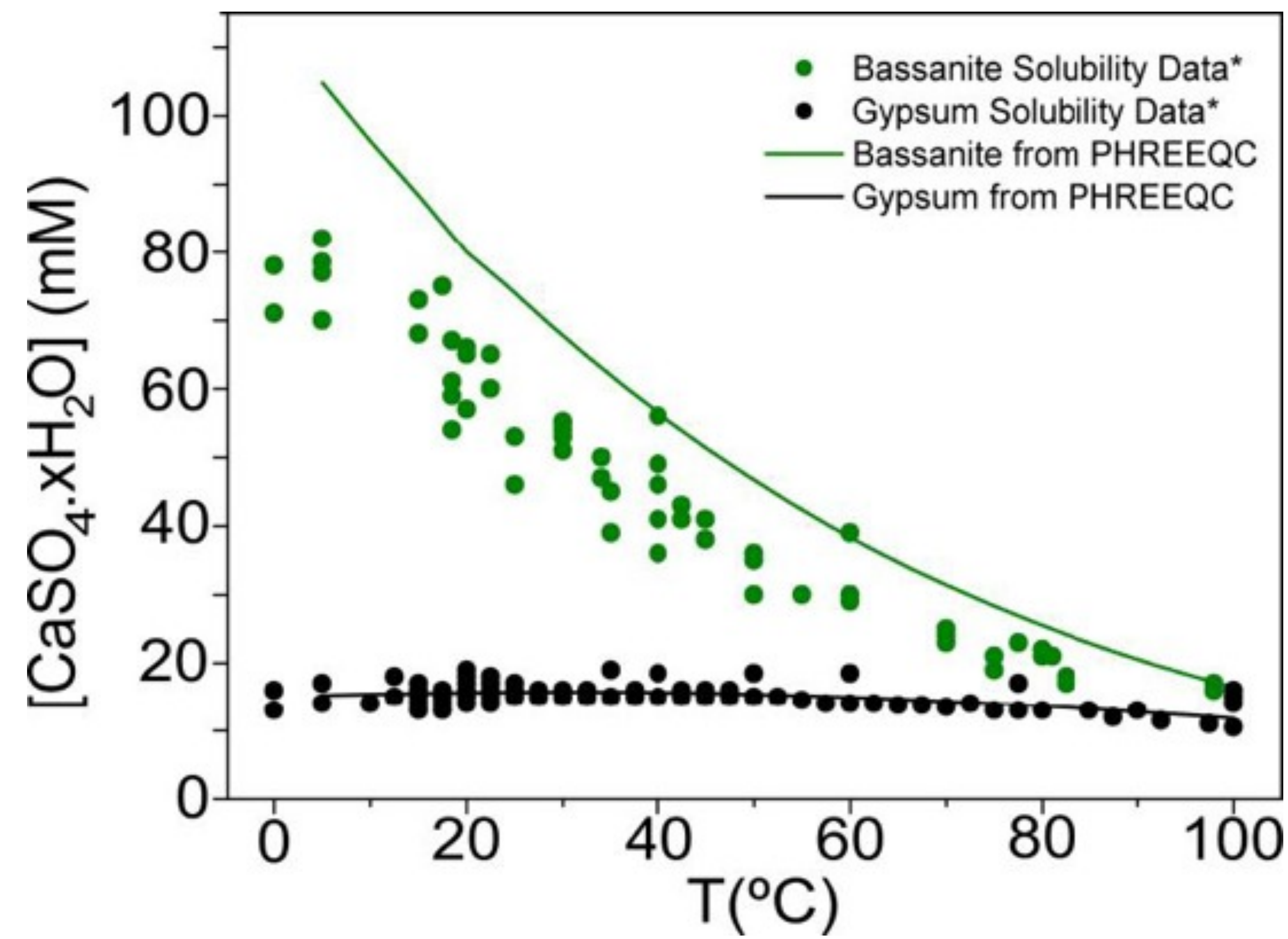
Anhidrite: $CaSO_4$

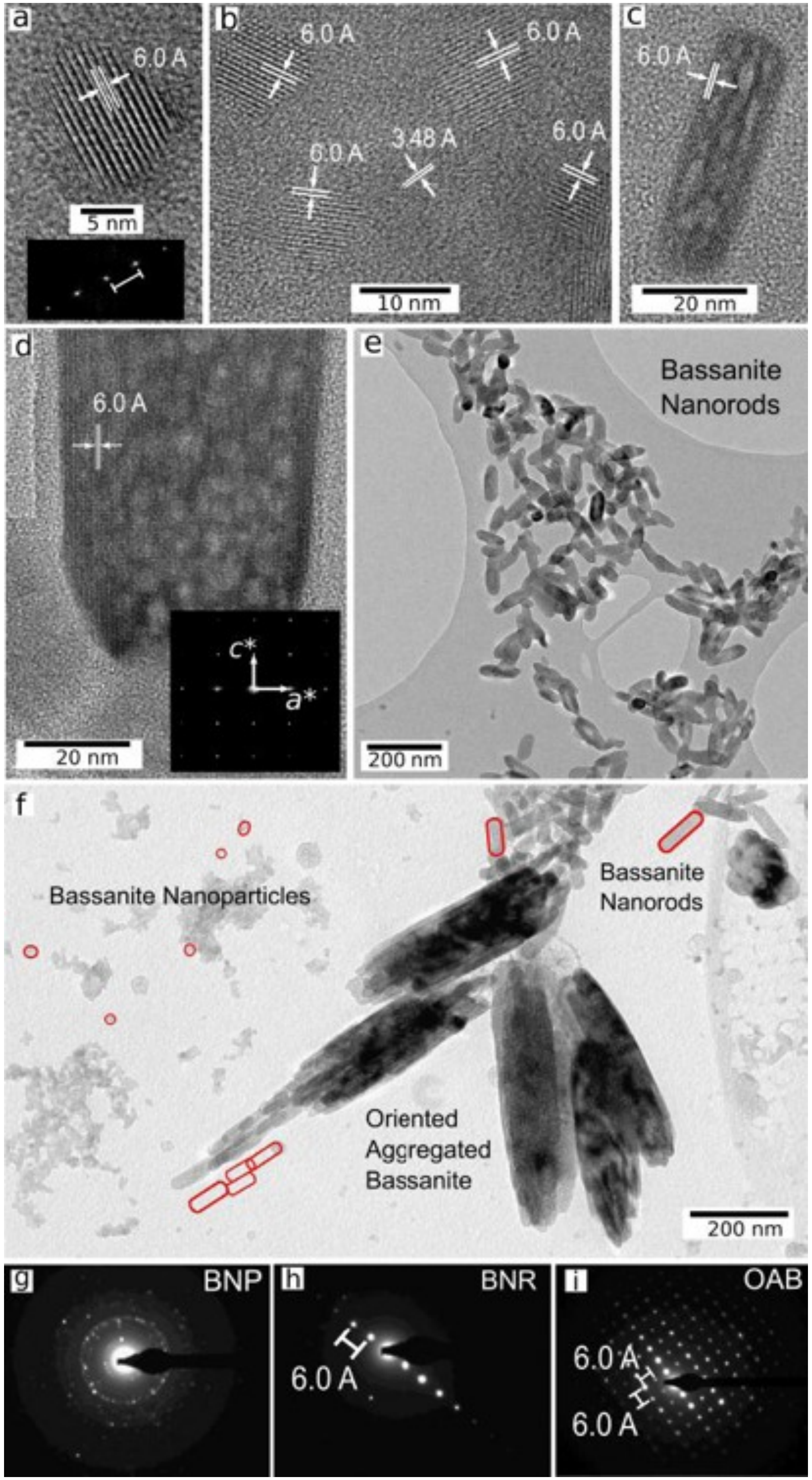
Orthorrombic
Point symmetry group (2/m 2/m 2/m)
Space symmetry group: Amma

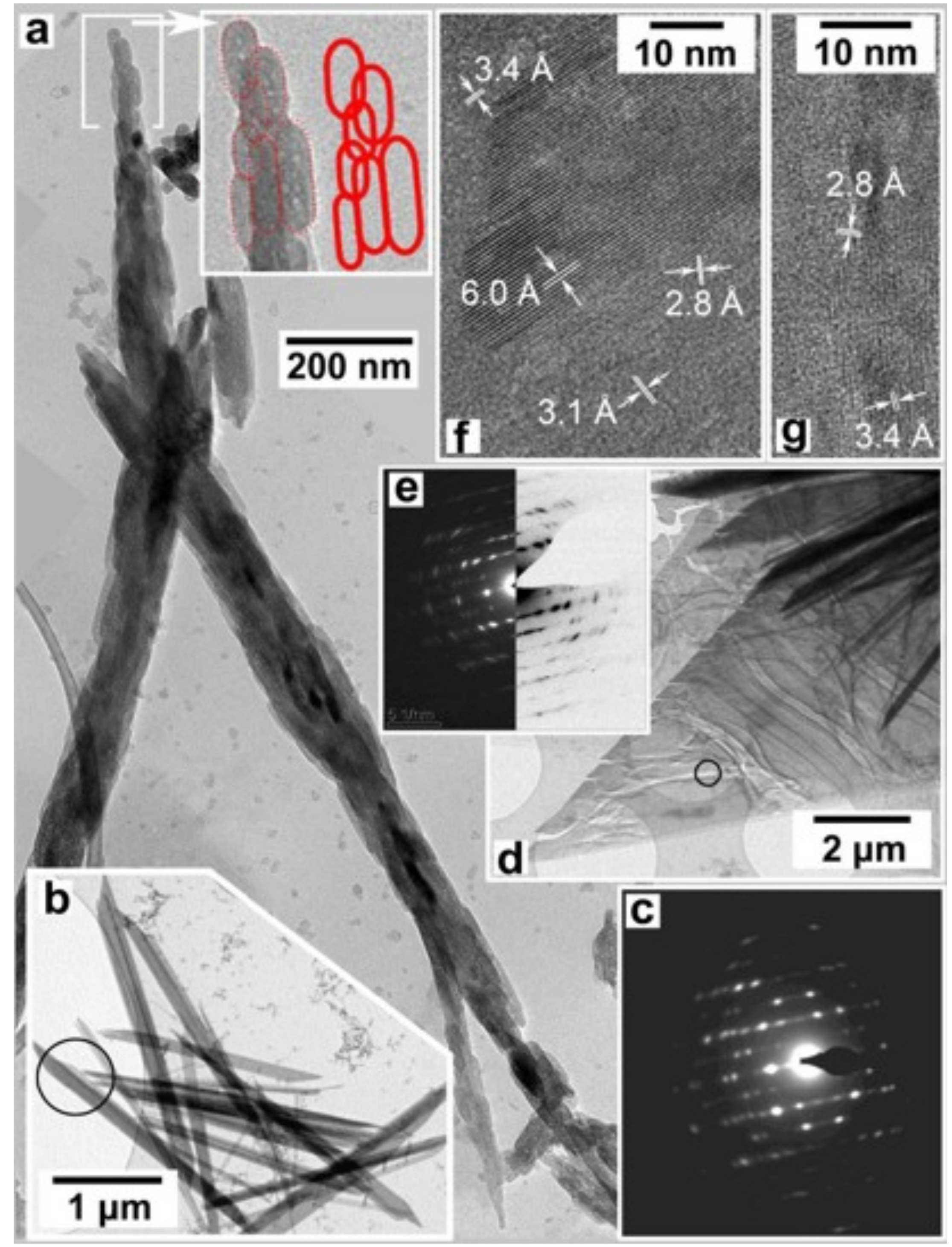
Bassanite: $CaSO_4 \cdot 1/2\,H_2O$

Monoclinic
Point symmetry group (2)
Space symmetry group: I2


a
Bassanite
Anhydrite
Gypsum
[CaSO4.xH2O] (mM)
T (ºC)
b
SIBas=0.18, SIGyp=1.04
Bassanite
SIBas=-0.02, SIGyp=0.84
SIBas=-0.16, SIGyp=0.70
SIBas=-0.37, SIGyp=0.50
Gypsum
SIBas=-0.72, SIGyp=0.14
[CaSO4.xH2O] (mM)
[Salinity (NaCl)] (mM)
c
Bassanite (constant γ)
Bassanite (decreasing γ)
Gypsum
Bassanite (negative γbulk)
bassanite to gypsum tranformation
oriented aggregation
nanoparticle formation and growth to nanorod
Enthalpy (kJ/mol)
bulk
nano
Surface Area (a.u.)


Bassanite Solubility Data*
Gypsum Solubility Data*
Bassanite from PHREEQC
Gypsum from PHREEQC
[CaSO4.xH2O] (mM)
T(ºC)


a
6.0 A
5 nm
b
6.0 A
6.0 A
6.0 A
3.48 A
6.0 A
10 nm
c
6.0 A
20 nm
d
6.0 A
c*
a*
20 nm
e
Bassanite
Nanorods
200 nm
f
Bassanite Nanoparticles
Bassanite
Nanorods
Oriented
Aggregated
Bassanite
200 nm
g
BNP
h
BNR
6.0 A
i
OAB
6.0 A
6.0 A


a
200 nm
10 nm
3.4 A
6.0 A
2.8 A
3.1 A
f
10 nm
2.8 A
3.4 A
g
e
d
2 μm
b
1 μm
c

- Precursors may form below their thermodynamic solubility curve.
- Precursors may have crystalline structures
- Self-assembled oriented aggregation may provoke phase transition

Live observation of precritical nuclei:

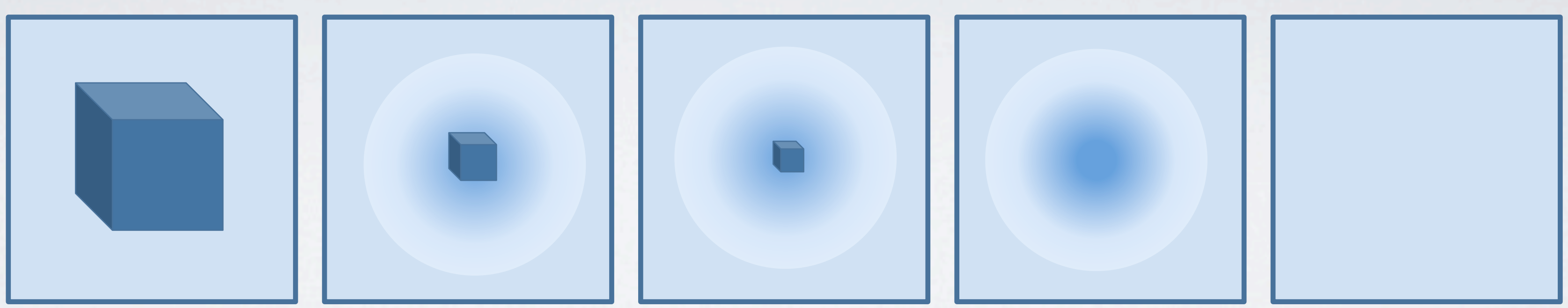
Submmited with Y. Kimura, H. Niinomi and K. Tsukamoto

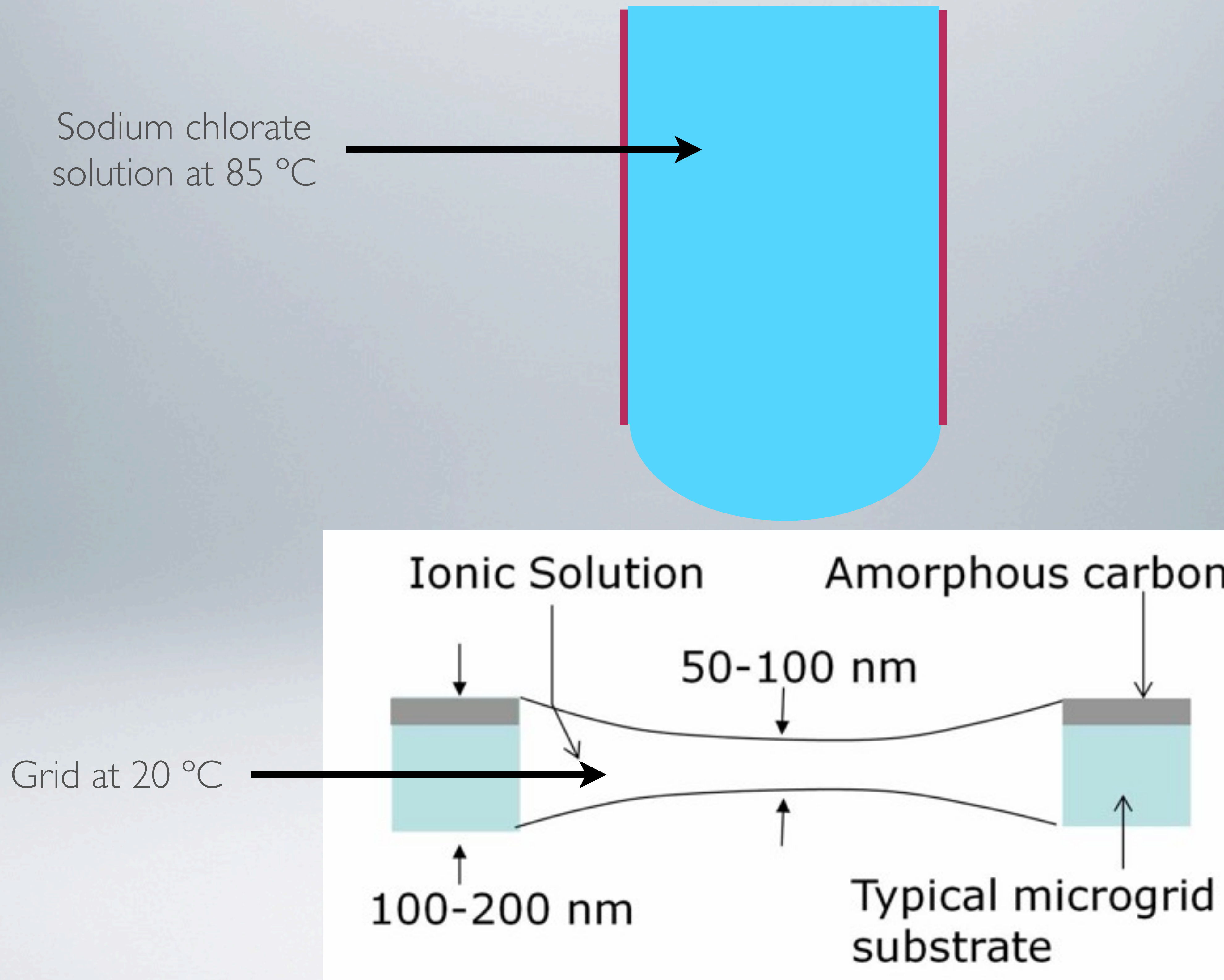
Tohoku University (Sendai, Japan)

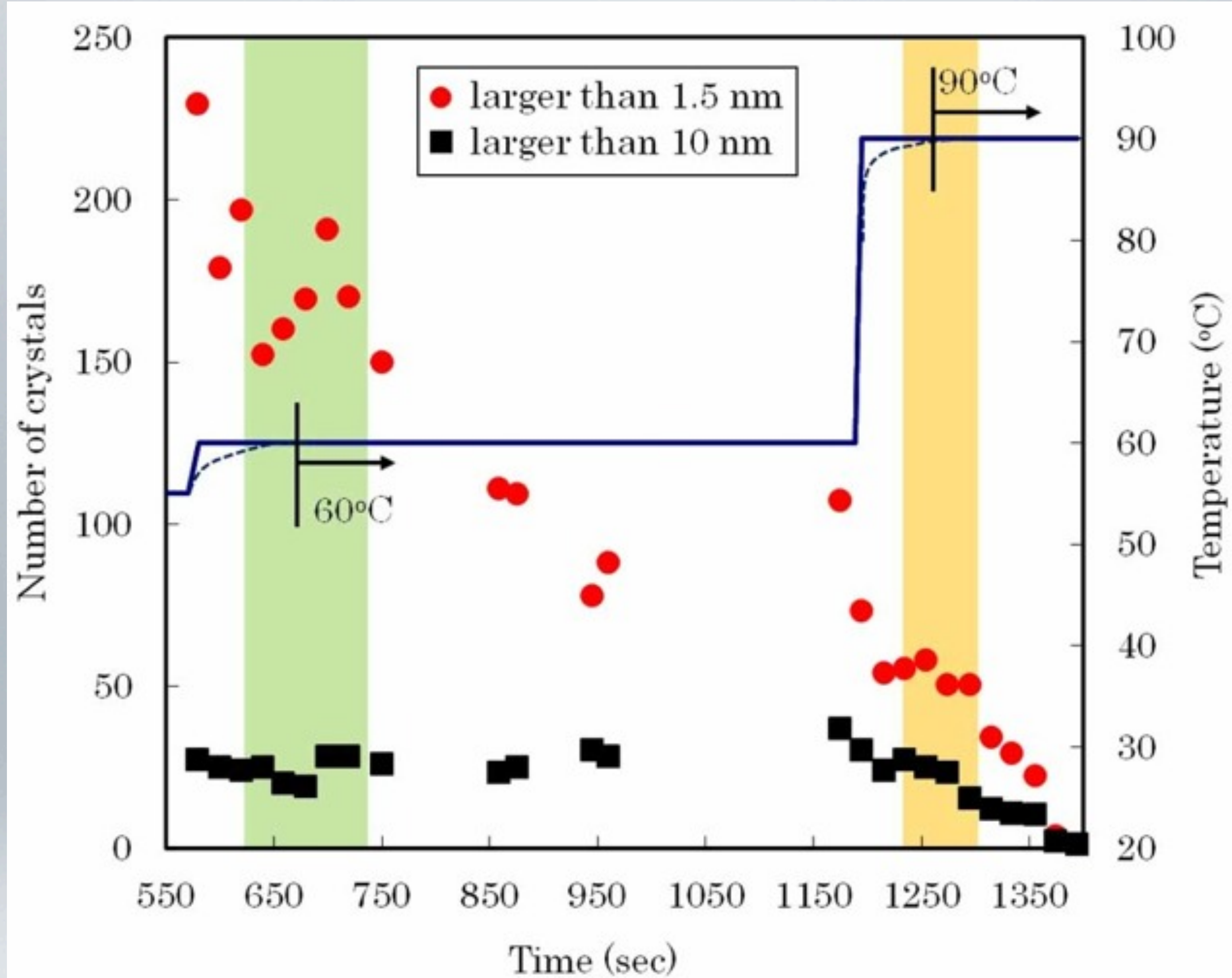
Search for precrítical nuclei within a very supersaturated solution is a problem because there should be millions of nuclei forming which make a problem of visualization.

Search for precrítical nuclei within a slightly supersaturated solution would be like looking for a needle in a haystack.

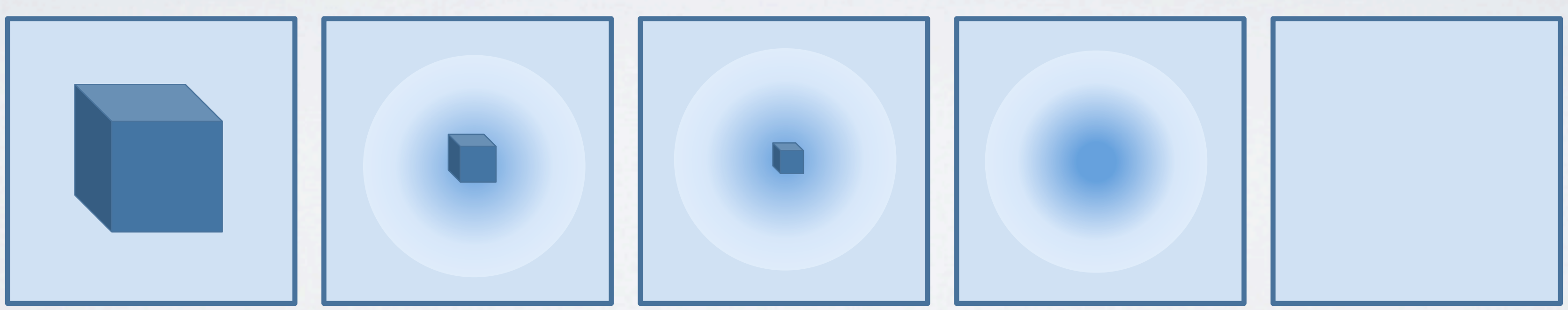
We tried an alternative route: search the saturated solution created around a dissolving cristal




Sodium chlorate
solution at 85 °C
Grid at 20 °C
Ionic Solution
Amorphous carbon
50-100 nm
100-200 nm
Typical microgrid
substrate



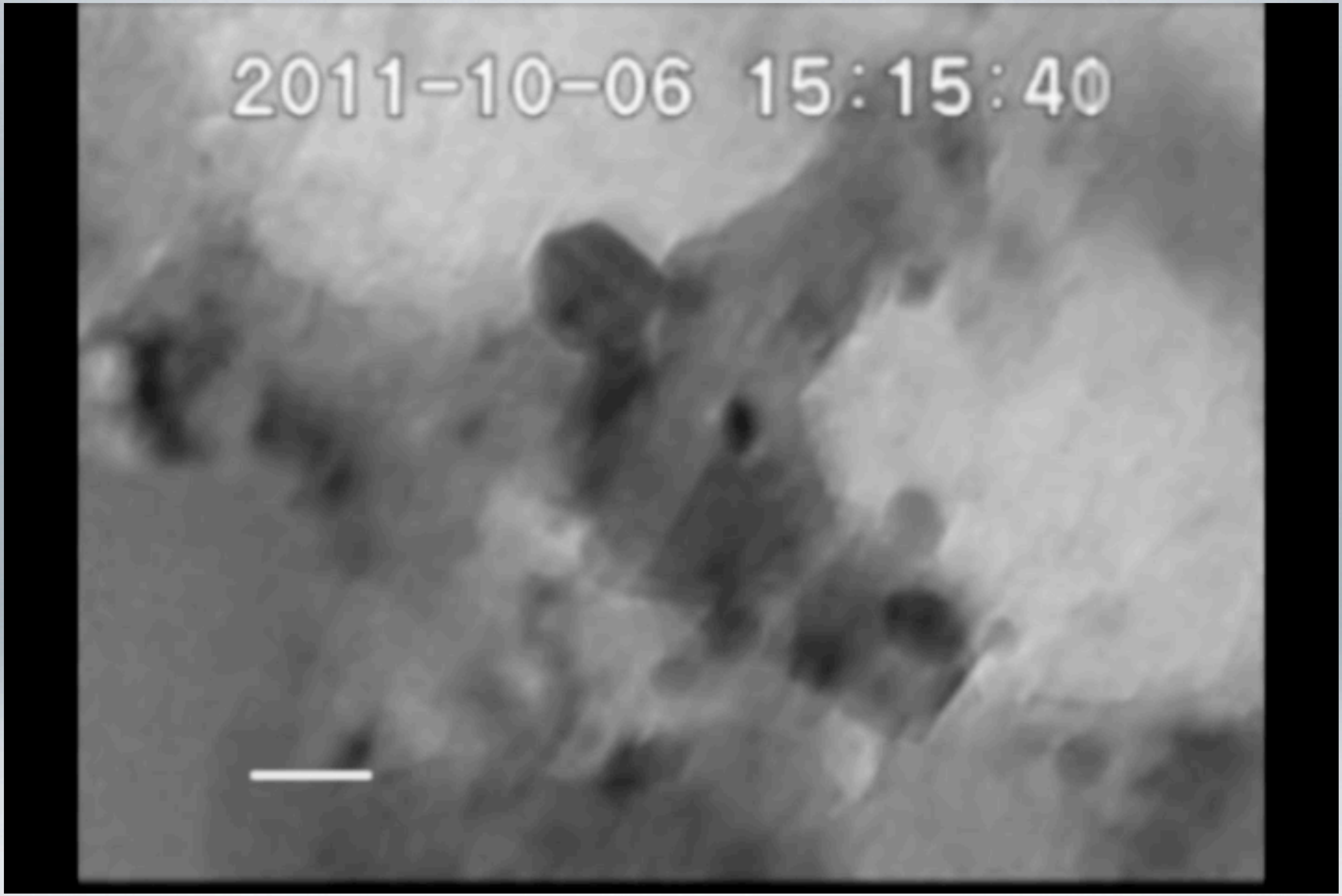
250
200
150
100
50
0
Number of crystals
larger than 1.5 nm
larger than 10 nm
60ºC
90ºC
100
90
80
70
60
50
40
30
20
Temperature (ºC)
550
650
750
850
950
1050
1150
1250
1350
Time (sec)



$NaClO_3$ crystals at 60ºC

scale bar 30 nm

Resolution : 0,7 nm



$NaClO_3$ crystals at 60°C

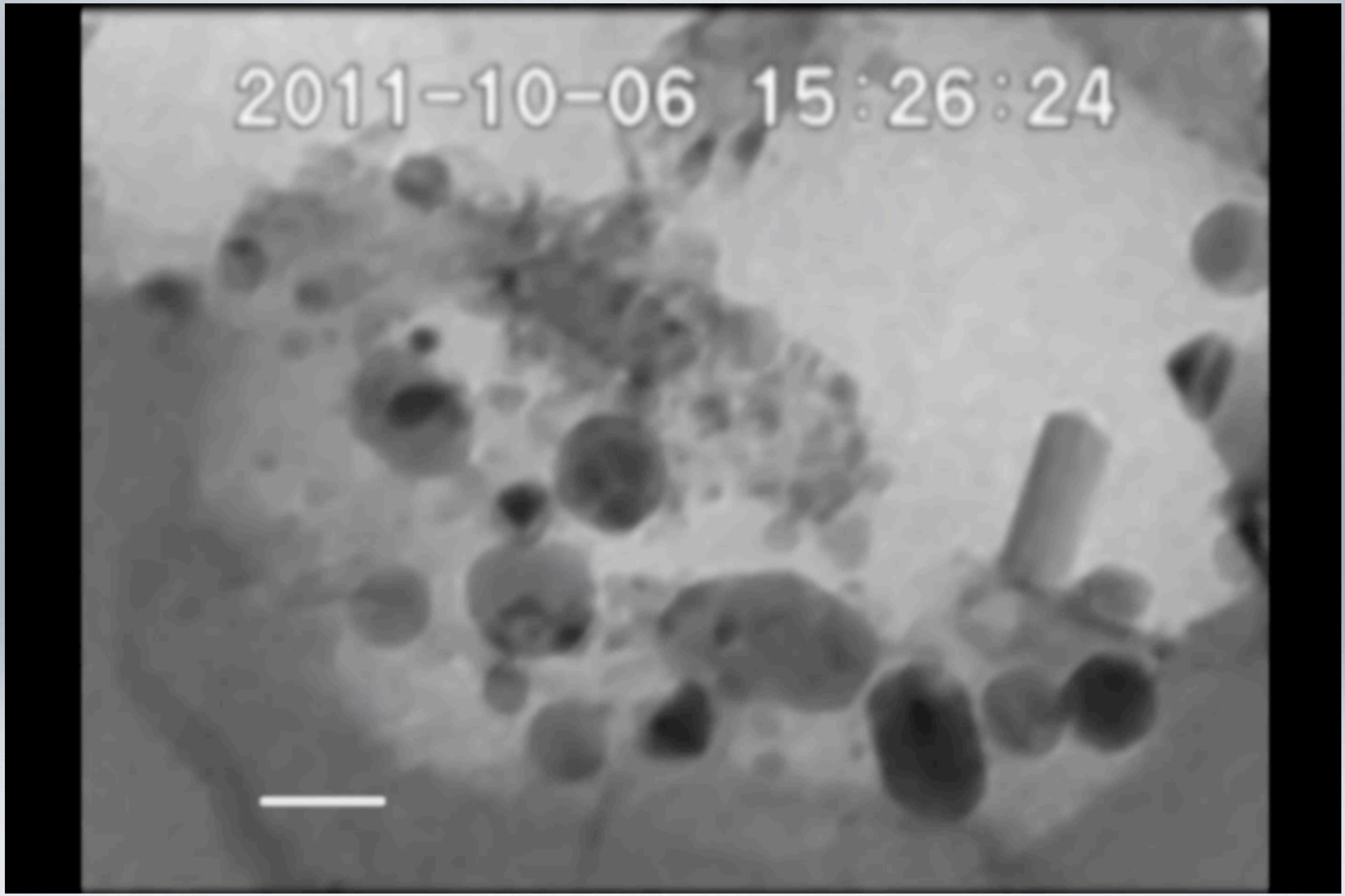
scale bar 30 nm

Resolution : 0,7 nm

NaClO3 crystals at 90ºC

scale bar 30 nm

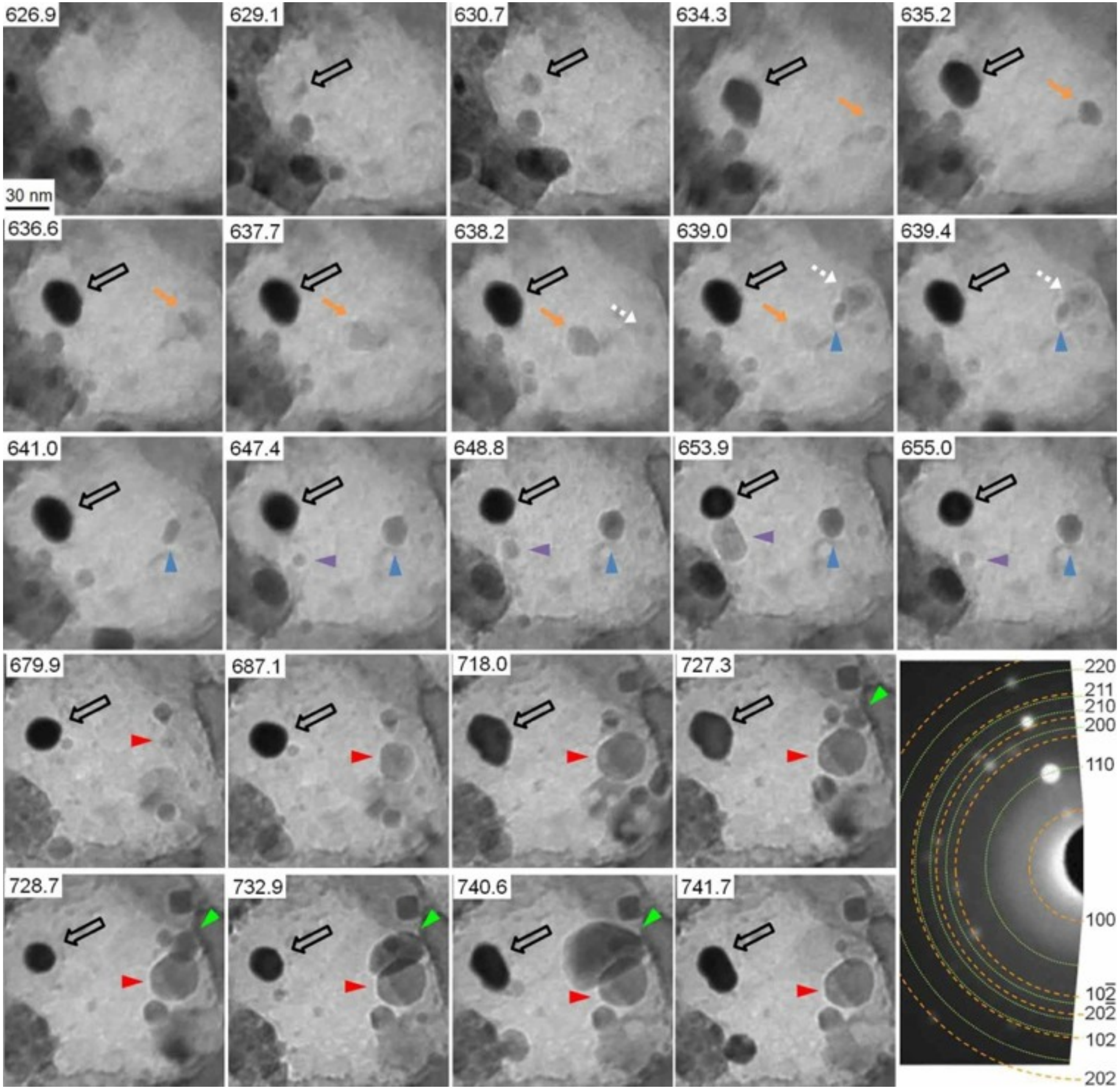
Resolution : 0,7 nm



NaClO3 crystals at 90°C

scale bar 30 nm

Resolution : 0,7 nm

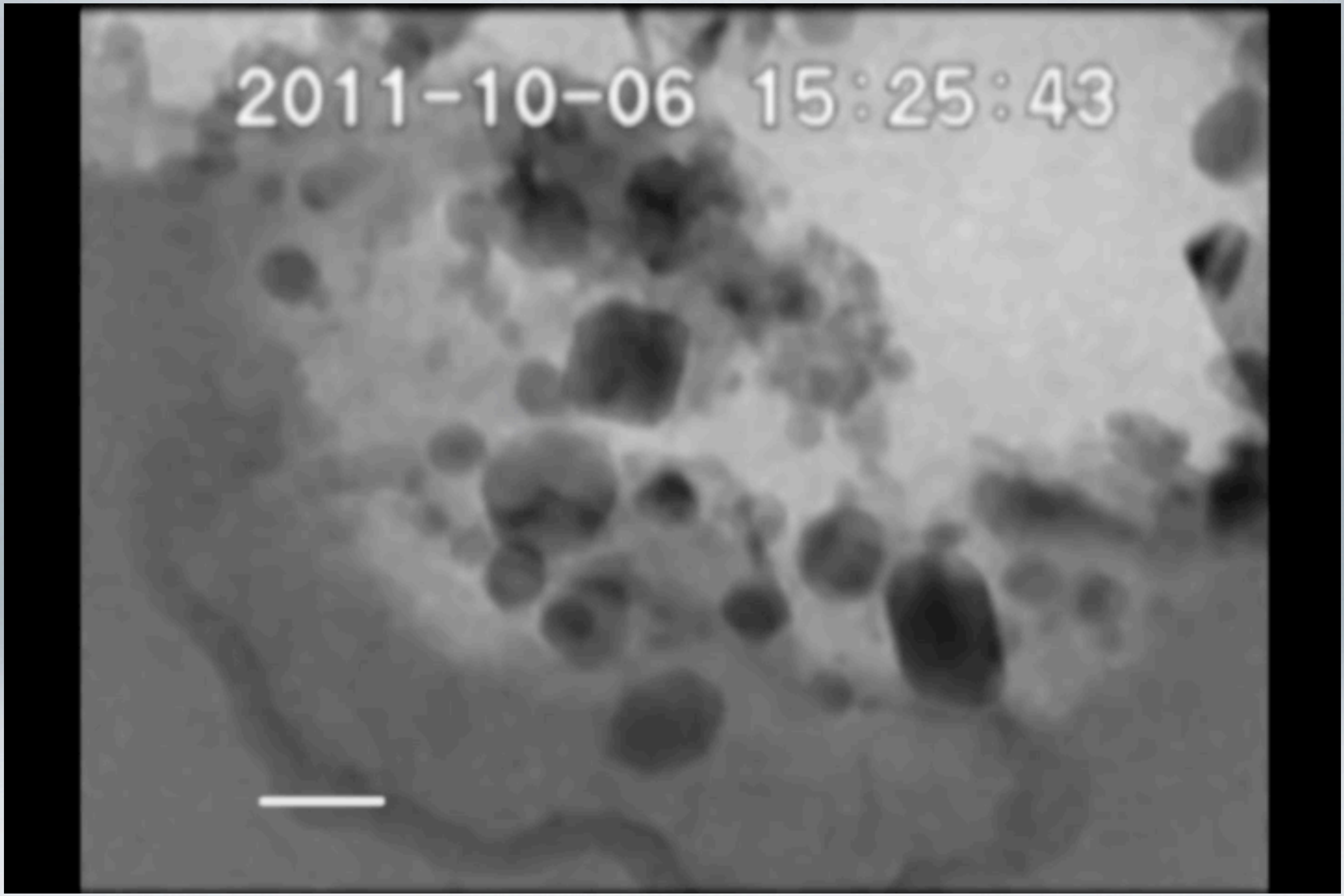


626.9
629.1
630.7
634.3
635.2
30 nm
636.6
637.7
638.2
639.0
639.4
641.0
647.4
648.8
653.9
655.0
679.9
687.1
718.0
727.3
728.7
732.9
740.6
741.7
220
211
210
200
110
100
10$\bar{2}$
20$\bar{2}$
102
202

$NaClO_3$ crystals at 90°C

scale bar 30 nm

Resolution : 0,7 nm



$NaClO_3$ crystals at 90°C

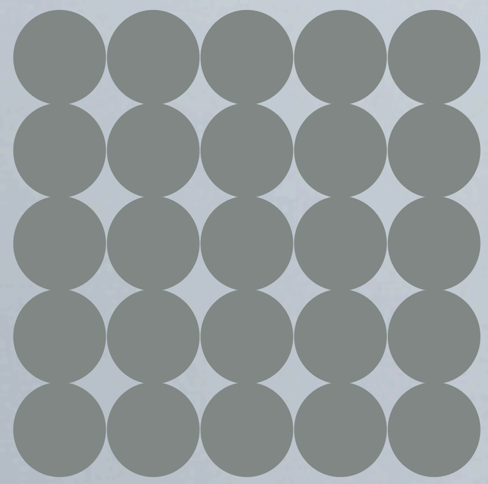
scale bar 30 nm

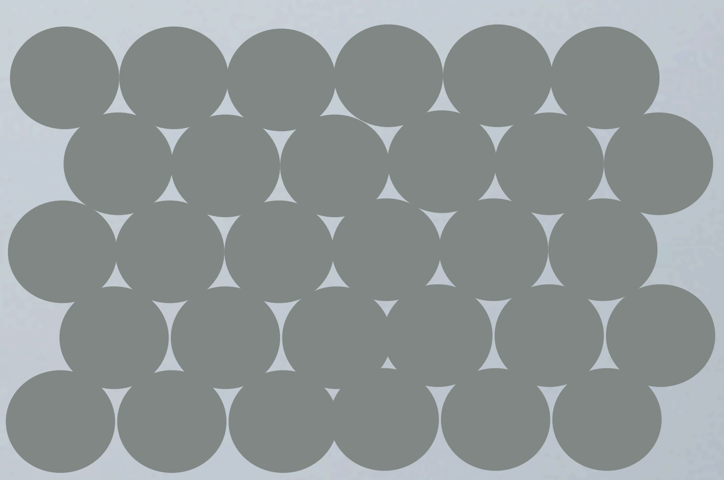
Resolution : 0,7 nm

The thermodynamic solubility does not control the formation of polymorphs. Both polymorph, low and high temperature are formed in the solution undersaturated!

Surface stability starts to be important as the clusters grow. It may be that both polymorphs or solvates exceed the critical size.

The compromise between structural disorder and aggregation disorder dictates the probability of formation of a given polymorphic configuration





Configurational order (how difficult is to arrange elemental units in these configurations)
vs
aggregation rate, i.e. how many particles and how fast meet in a given locality

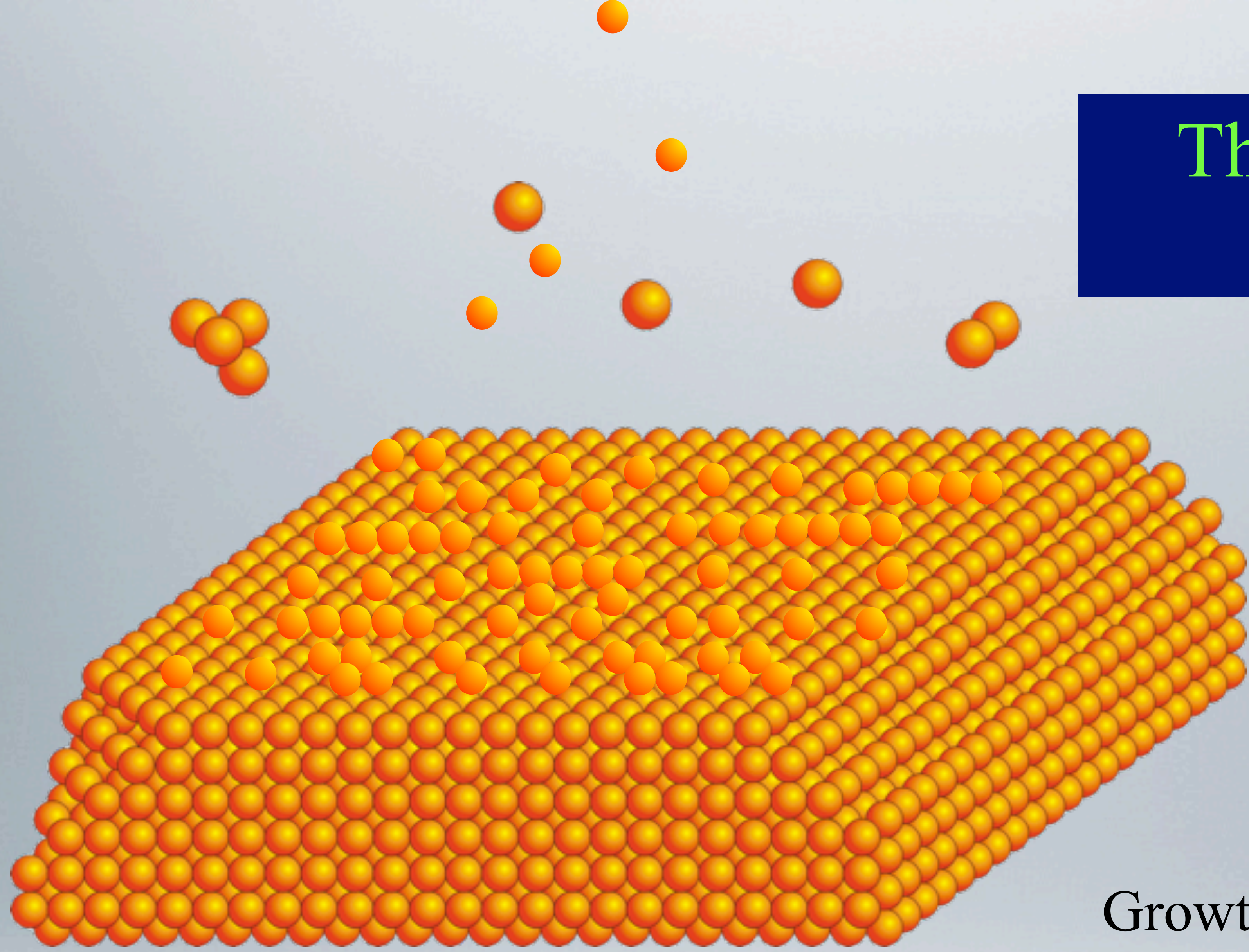
Crystal Growth Mechanisms
Normal Growth
(Direct Accretion)

Crystals grow by accretion of growth units

GU can be atoms, anionic or polyanionic species, or their clusters

The GU are acretted to the crystal by different mechanisms

Growth mechanisms may work simultaneously, so the faster mechanism dominates the overal growth rate

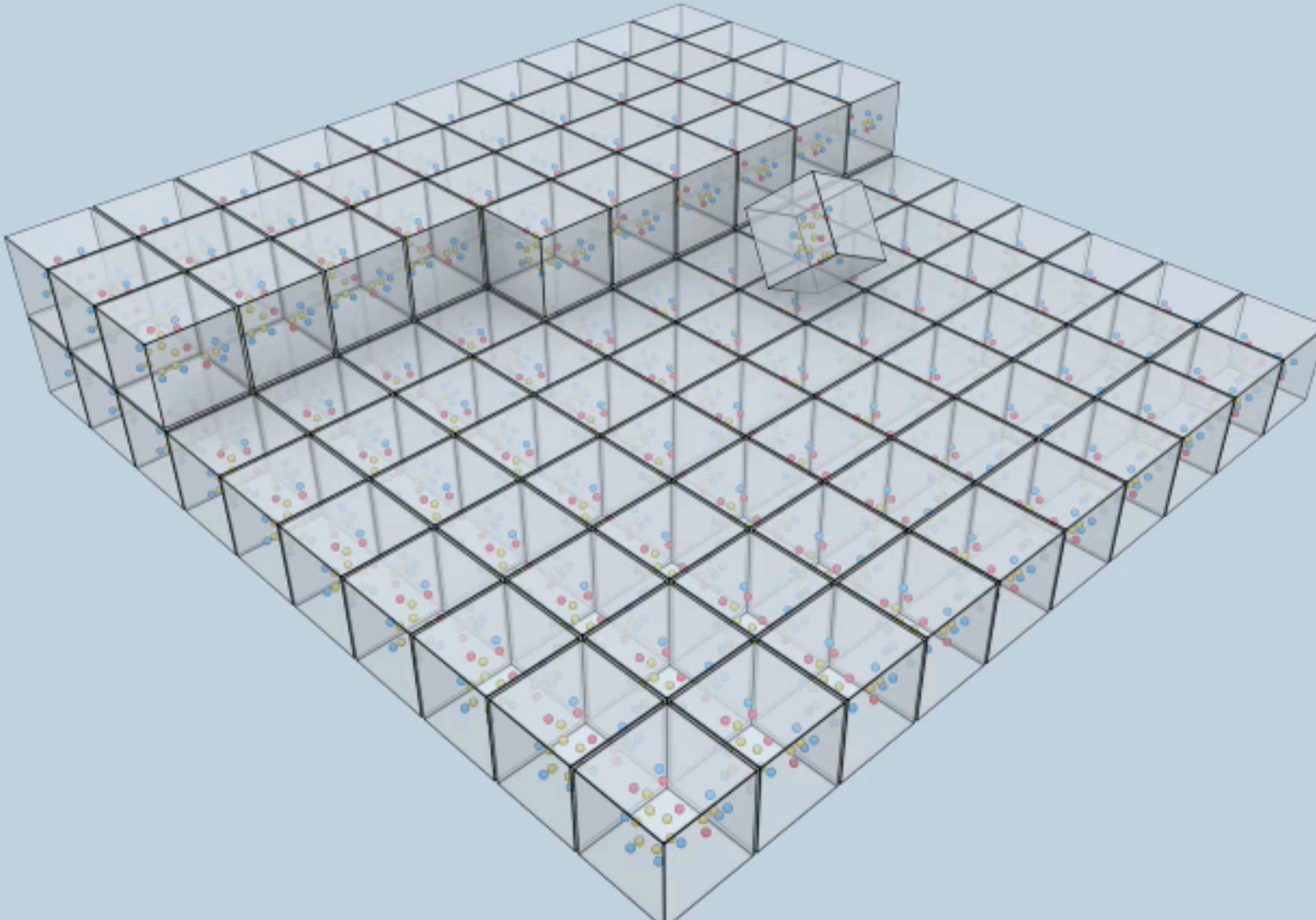


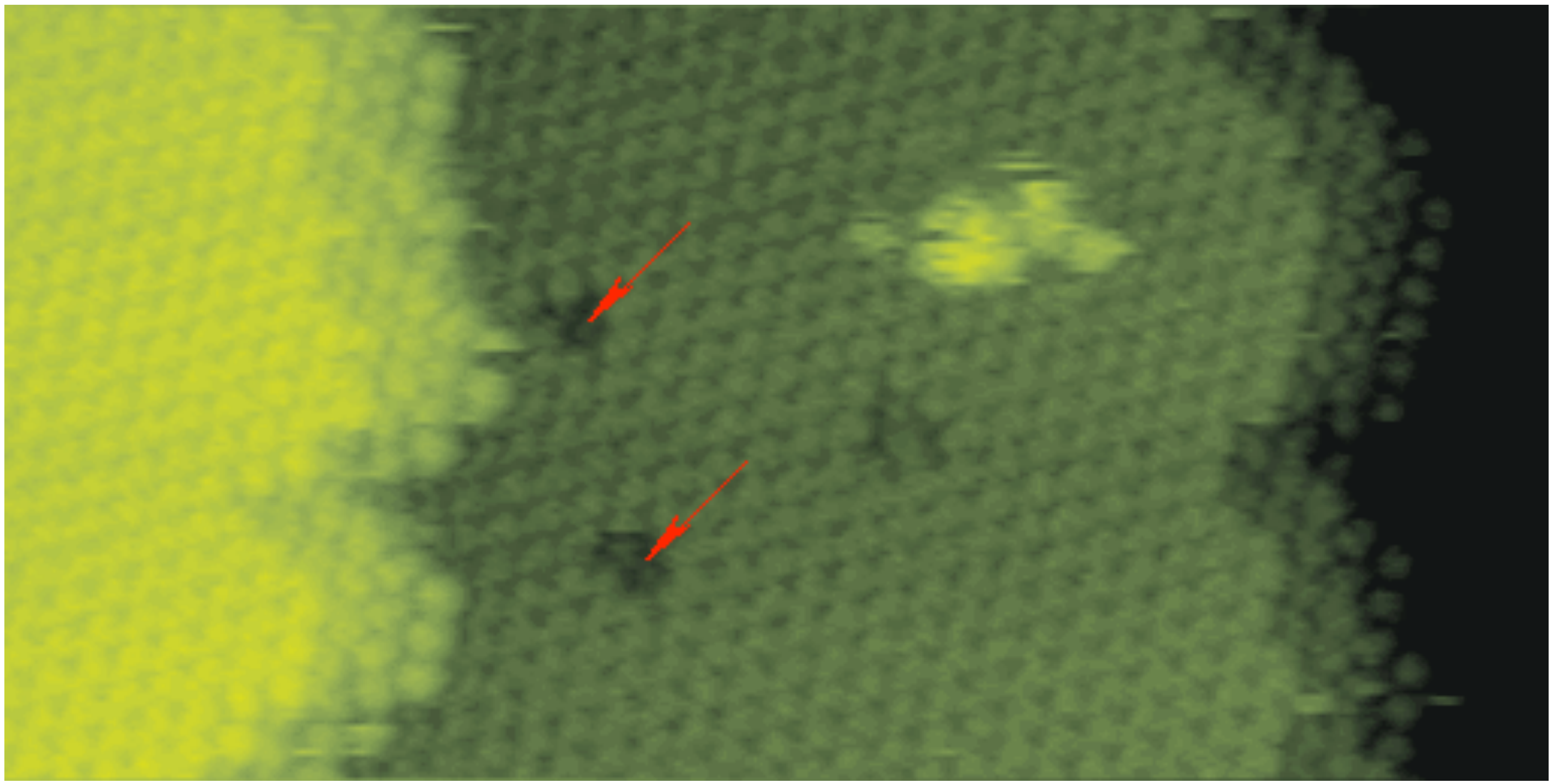
The growth of a rough crystal surface

Growth by direct accretion:
Normal growth

$$R_g = k(\sigma - 1) = k\beta$$

Linear trend with supersaturation



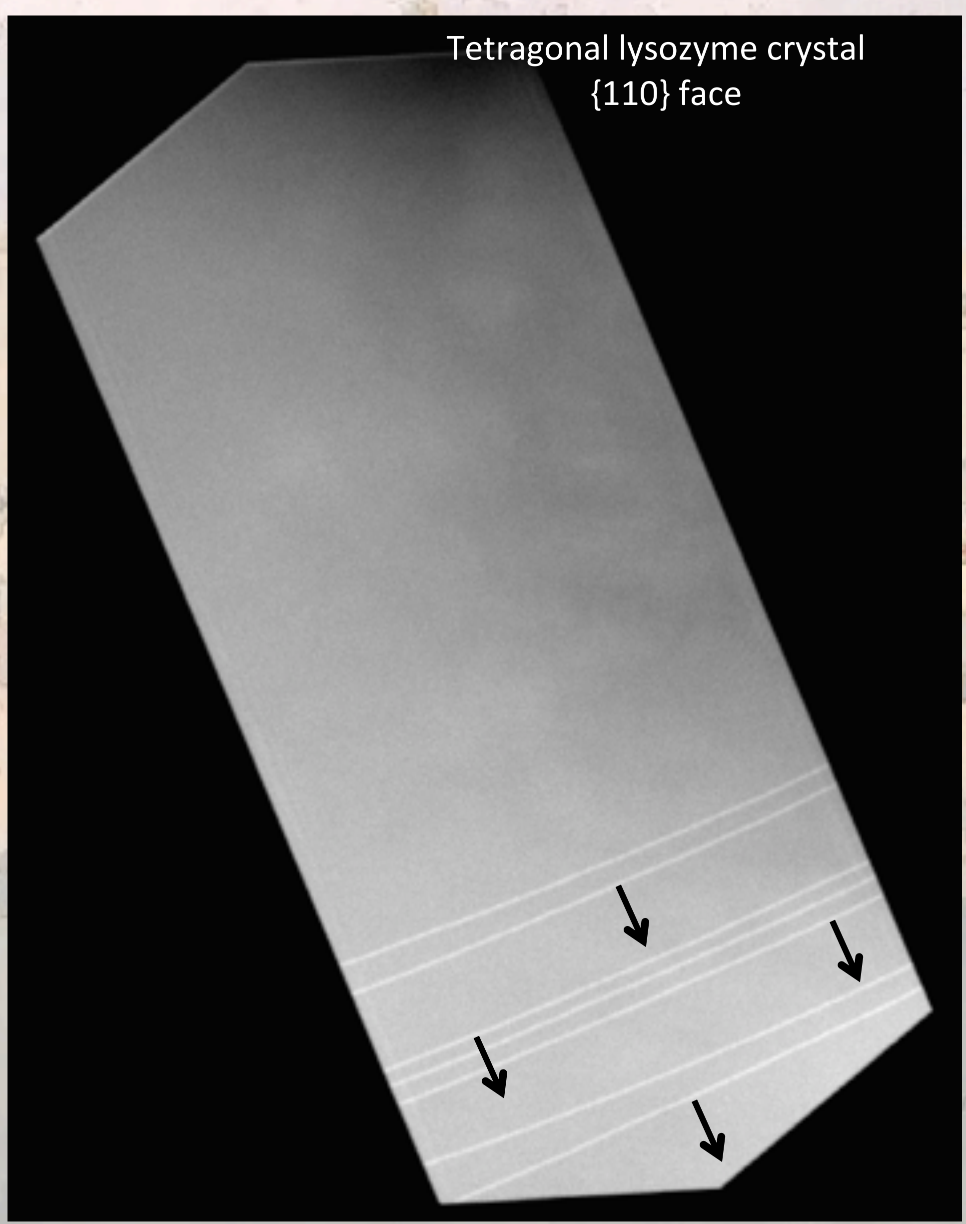


Movie provided by Peter Vekilov and Georgiou

→ Layer-wise growth occurs through the advancement of steps parallel to the crystal surface (= tangential growth)

→ Layer-wise growth occurs through the advancement of steps parallel to the crystal surface (= tangential growth)

→ Layer-wise growth occurs through the advancement of steps parallel to the crystal surface (= tangential growth)

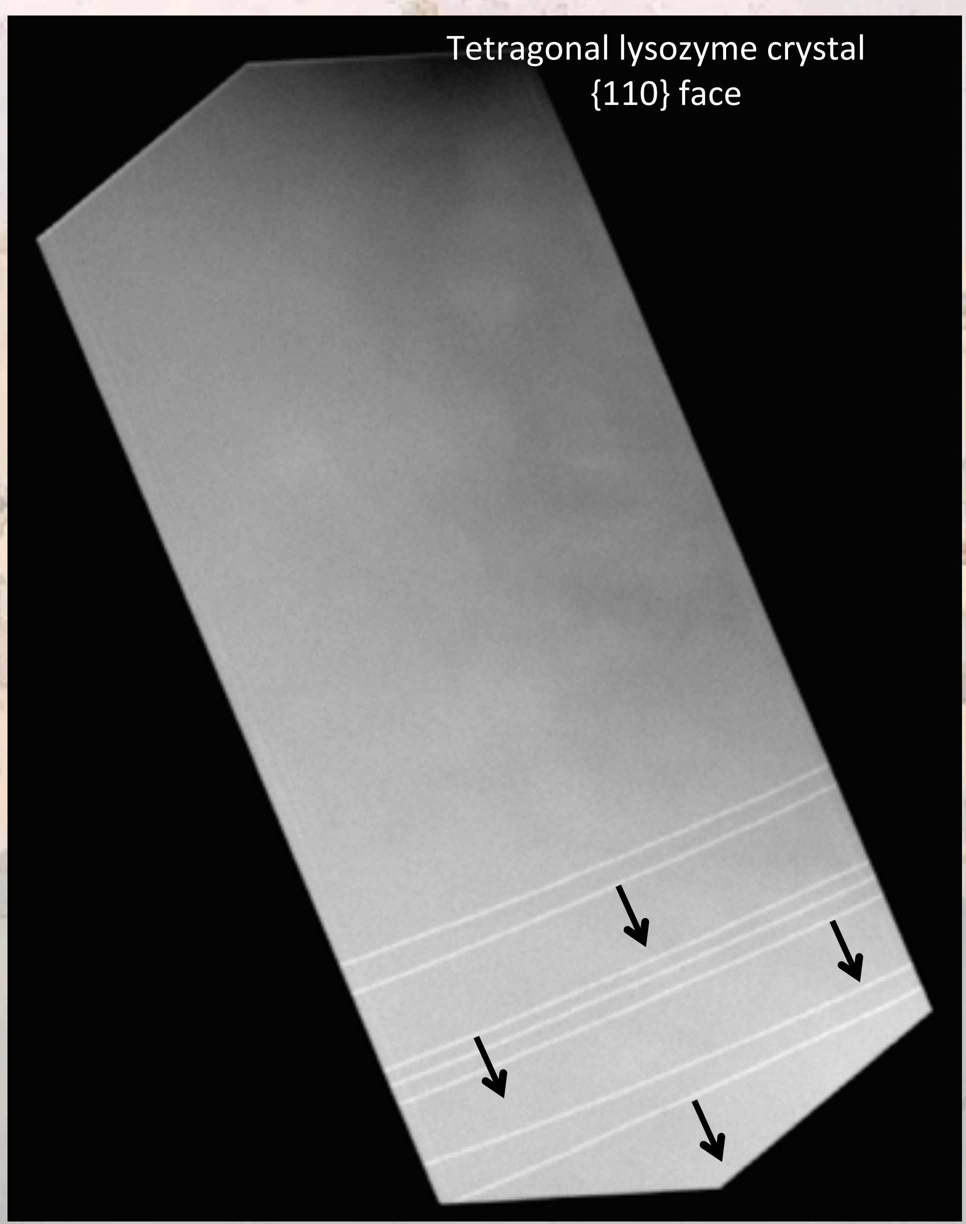


→ Layer-wise growth occurs through the advancement of steps parallel to the crystal surface (= tangential growth)

→ Upon reaching the edge of the crystal face, the layer is completed and the step disappears.

→ Layer-wise growth occurs through the advancement of steps parallel to the crystal surface (= tangential growth)

→ Upon reaching the edge of the crystal face, the layer is completed and the step disappears.

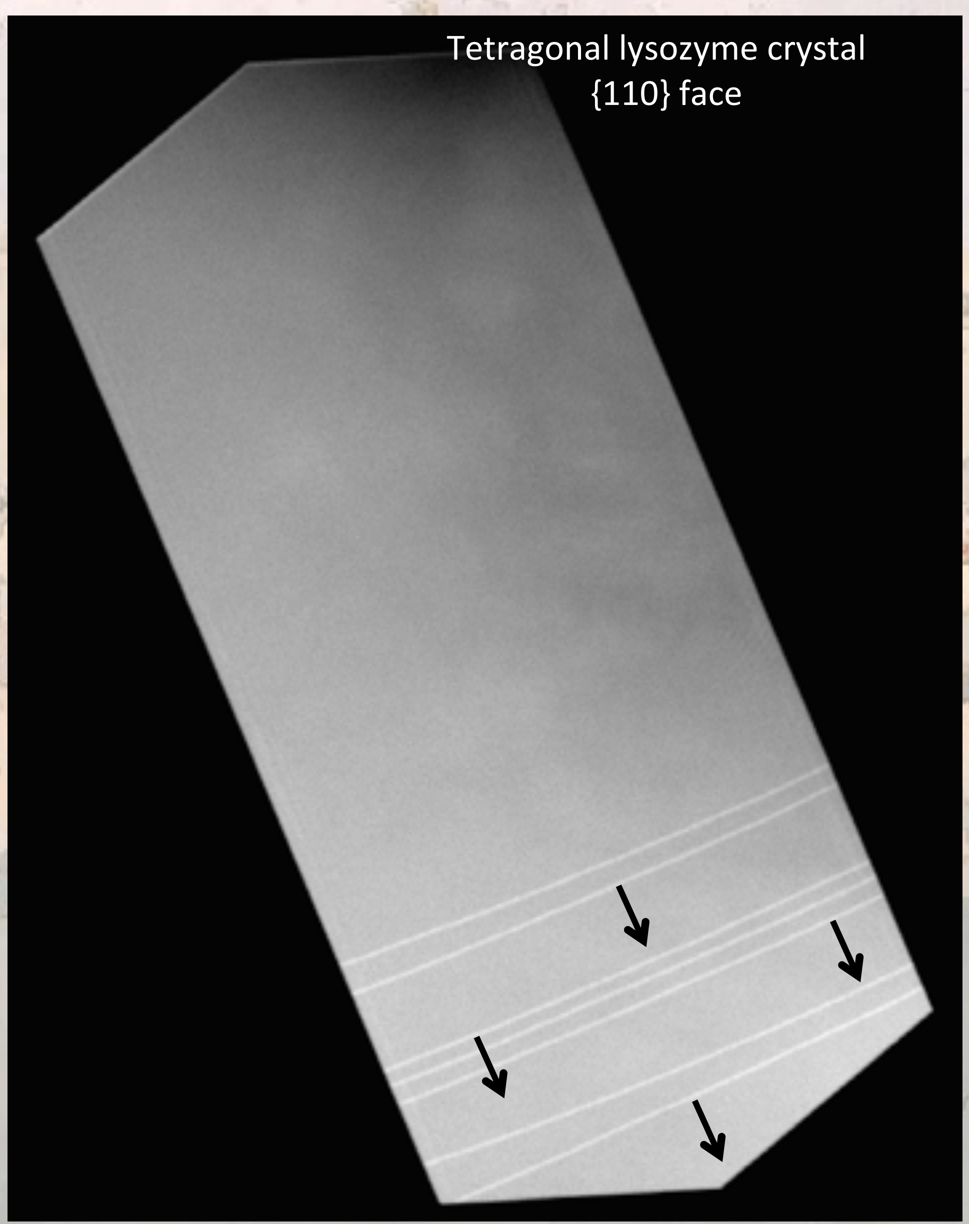


To continue growth ad infinitum, new layers need to be generated

Growth mechanisms

→ Layer-wise growth occurs through the advancement of steps parallel to the crystal surface (= tangential growth)

→ Upon reaching the edge of the crystal face, the layer is completed and the step disappears.



To continue growth ad infinitum, new layers need to be generated

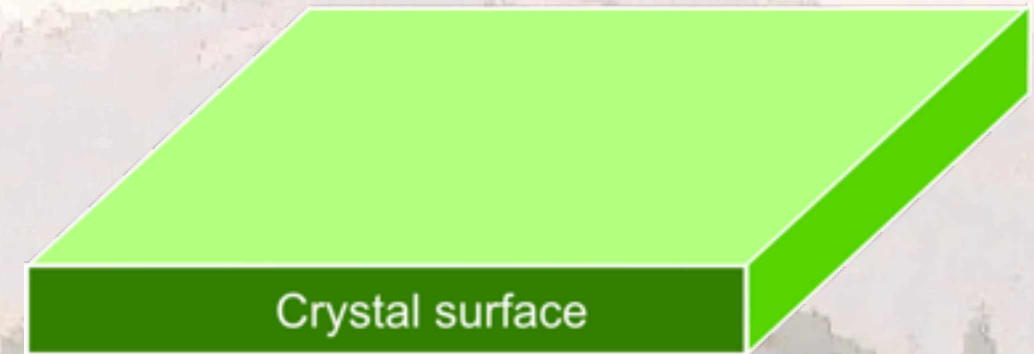
Growth mechanisms

The creation of layers advances the crystal face normal to its average direction (= normal growth)

Crystal Growth Mechanisms
Two-dimensional nucleation

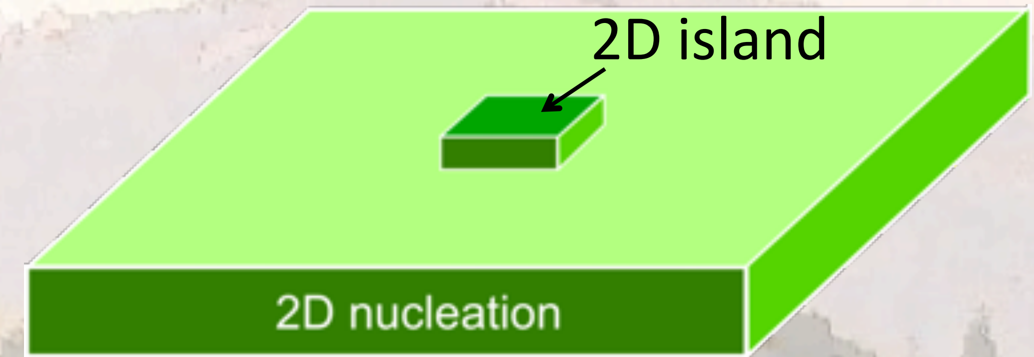
(Birth and Spread growth)

So what happens on perfect flat faces?



(Birth and Spread growth)

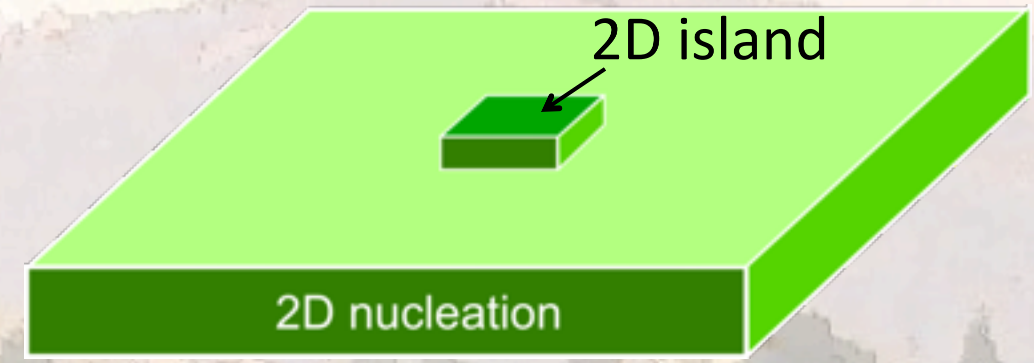
So what happens on perfect flat faces?



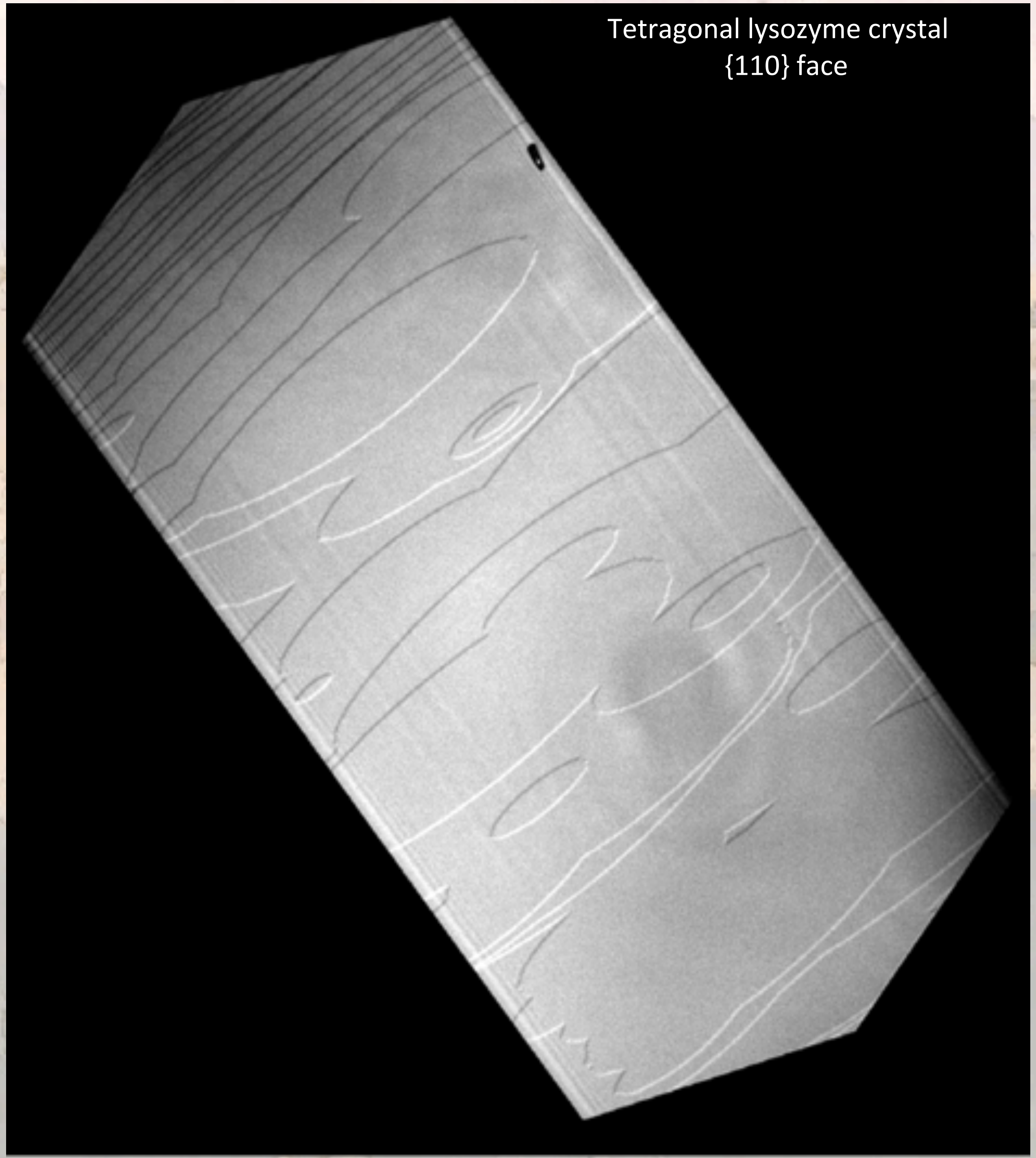
Steps are created by a process of two-dimensional nucleation: (≈3D nucleation)

(Birth and Spread growth)

So what happens on perfect flat faces?

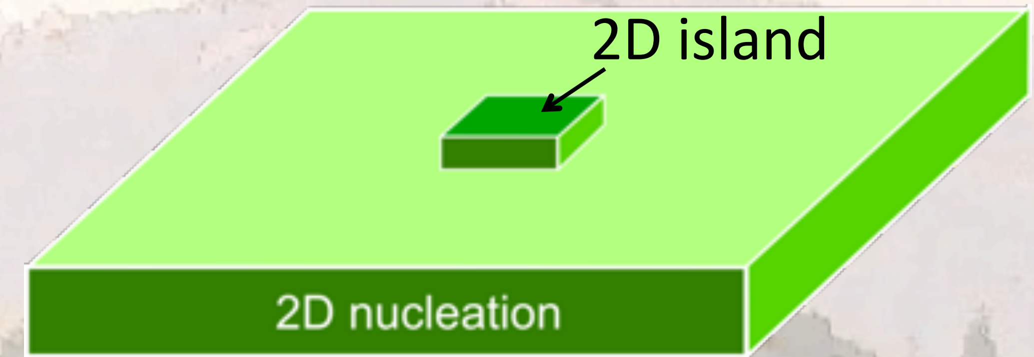


Steps are created by a process of two-dimensional nucleation: (≈3D nucleation)



(Birth and Spread growth)

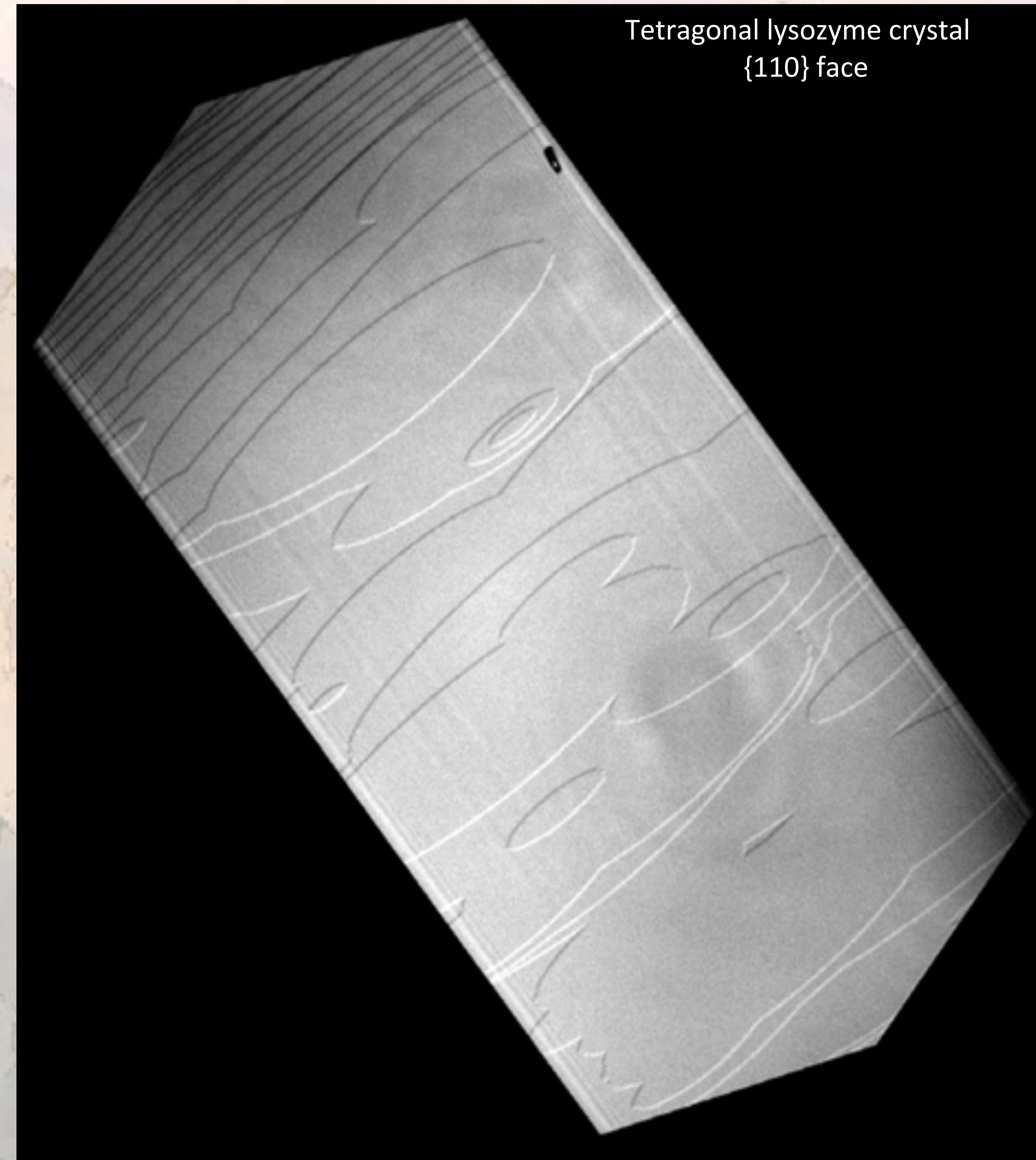
So what happens on perfect flat faces?



Steps are created by a process of two-dimensional nucleation: (≈3D nucleation)

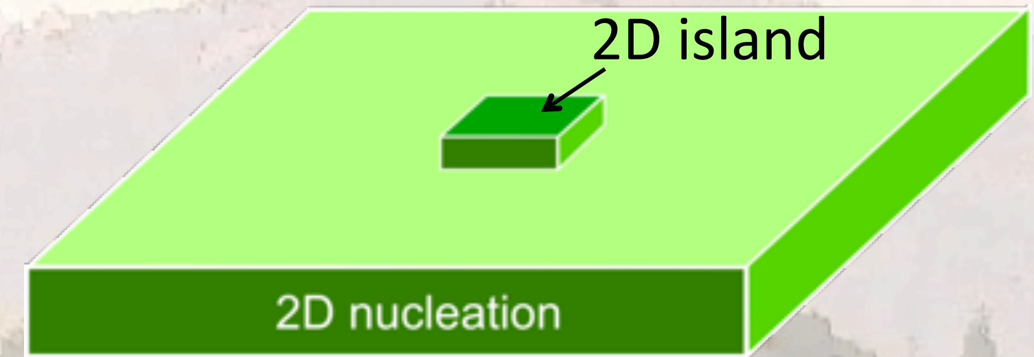
→ Nucleation barrier is involved

→ Mininum supersaturation is required



(Birth and Spread growth)

So what happens on perfect flat faces?

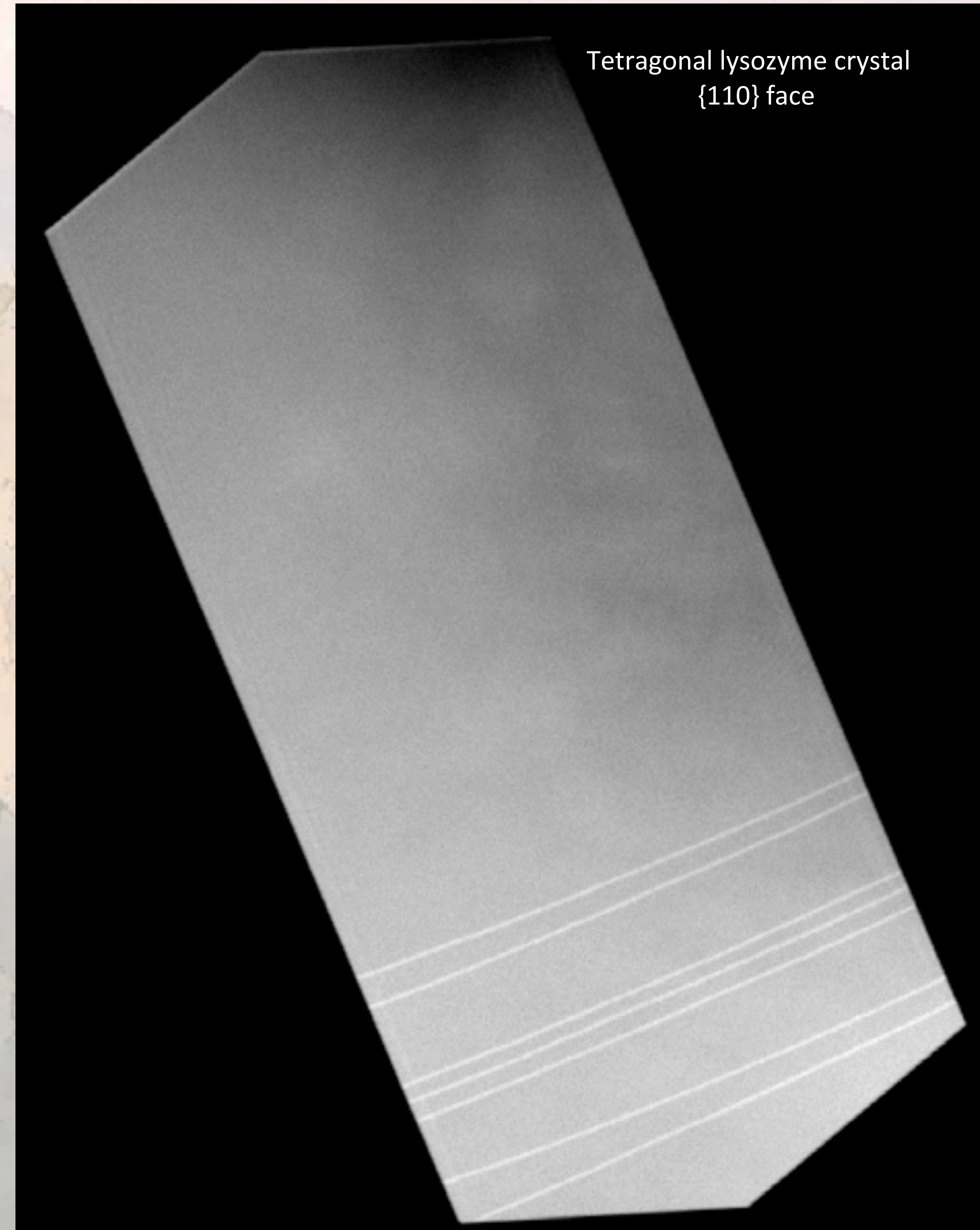


Steps are created by a process of two-dimensional nucleation: (≈3D nucleation)

→ Nucleation barrier is involved

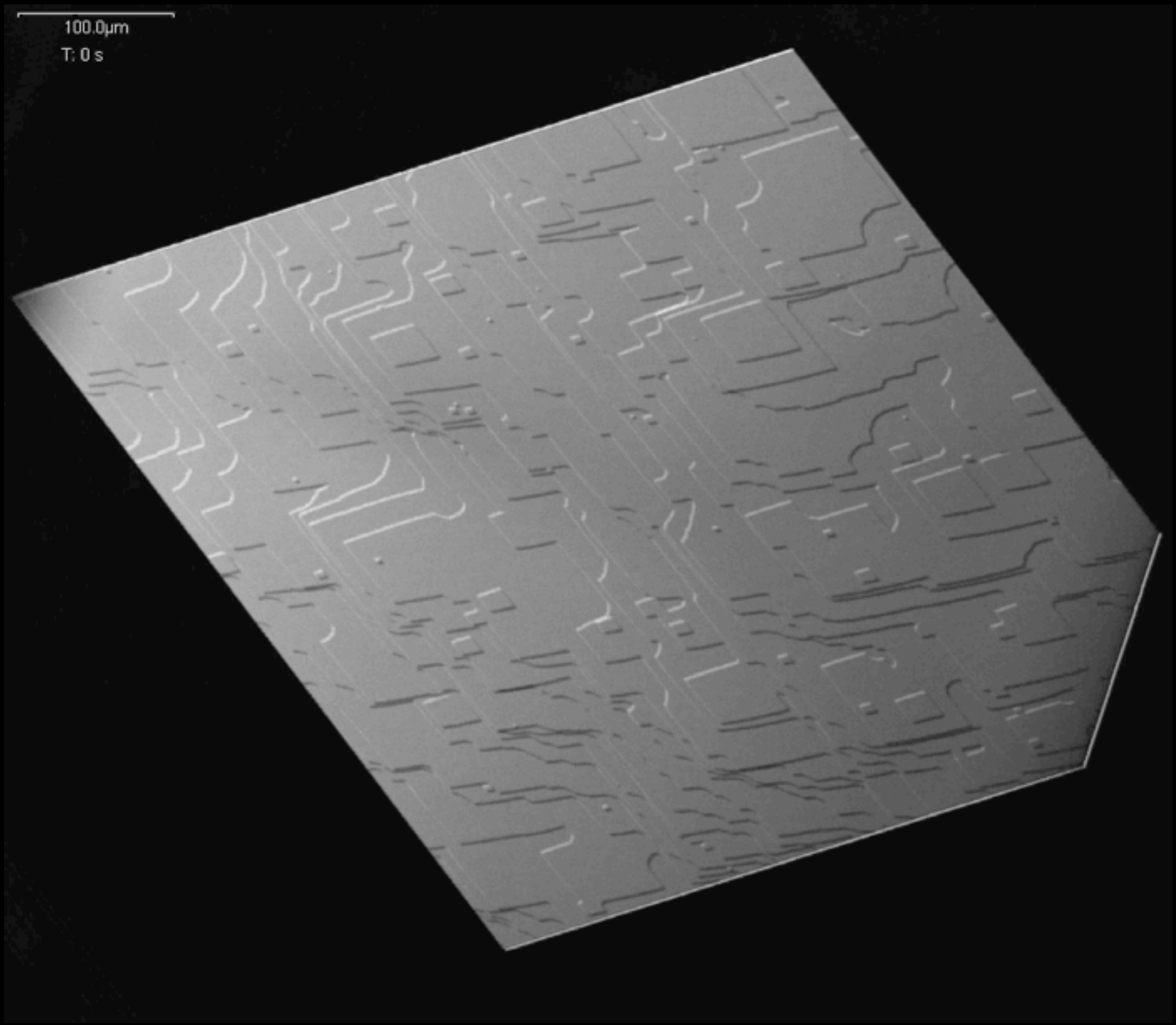
→ Mininum supersaturation is required

Below a critical driving force no 2D nuclei will form…

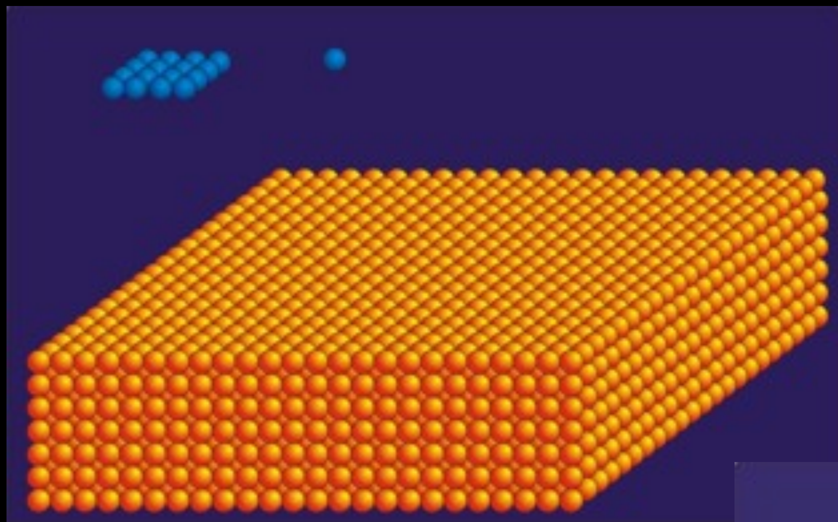


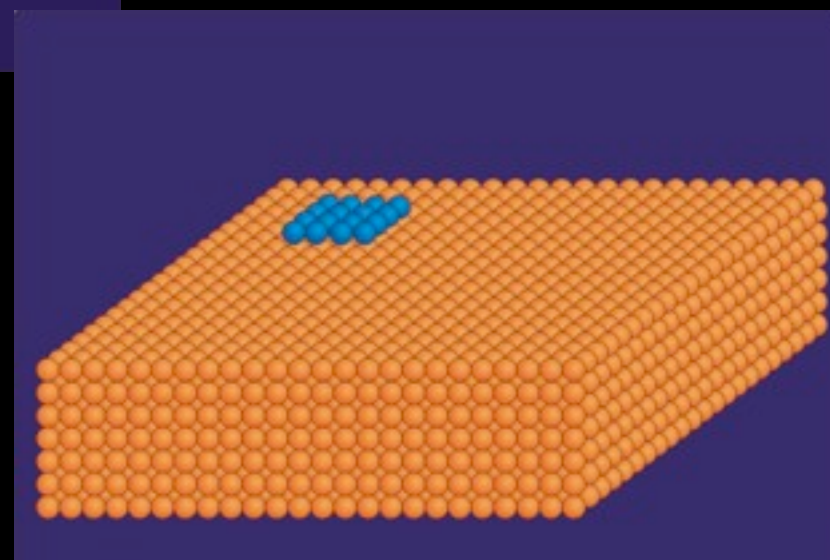
Juan Manuel García-Ruiz

Two dimensional nucleation



Growth by two-dimensional nucleation





$$\Delta G = 4n^{1/2}a^2\sigma - nKT\ln S$$

$$n* = \left[\frac{2a^2\sigma}{KT\ln S}\right]^2$$

$$\Delta G^* = \frac{4a^4\sigma^2}{KT\ln S}$$

$$P = \exp\left(\frac{-\Delta G^*}{KT}\right) = \exp\left[\frac{-\left(2a^{2\sigma}/KT\right)^2}{\ln S}\right]$$

$$v = k_{2D}\sigma^{5/6}\exp\left[\left(-\frac{\pi}{3\sigma}\right)\left(\frac{\gamma_e}{kT}\right)^2\right] = k_{2D}\sigma^{5/6}\exp\left(-\frac{B}{\sigma}\right)$$

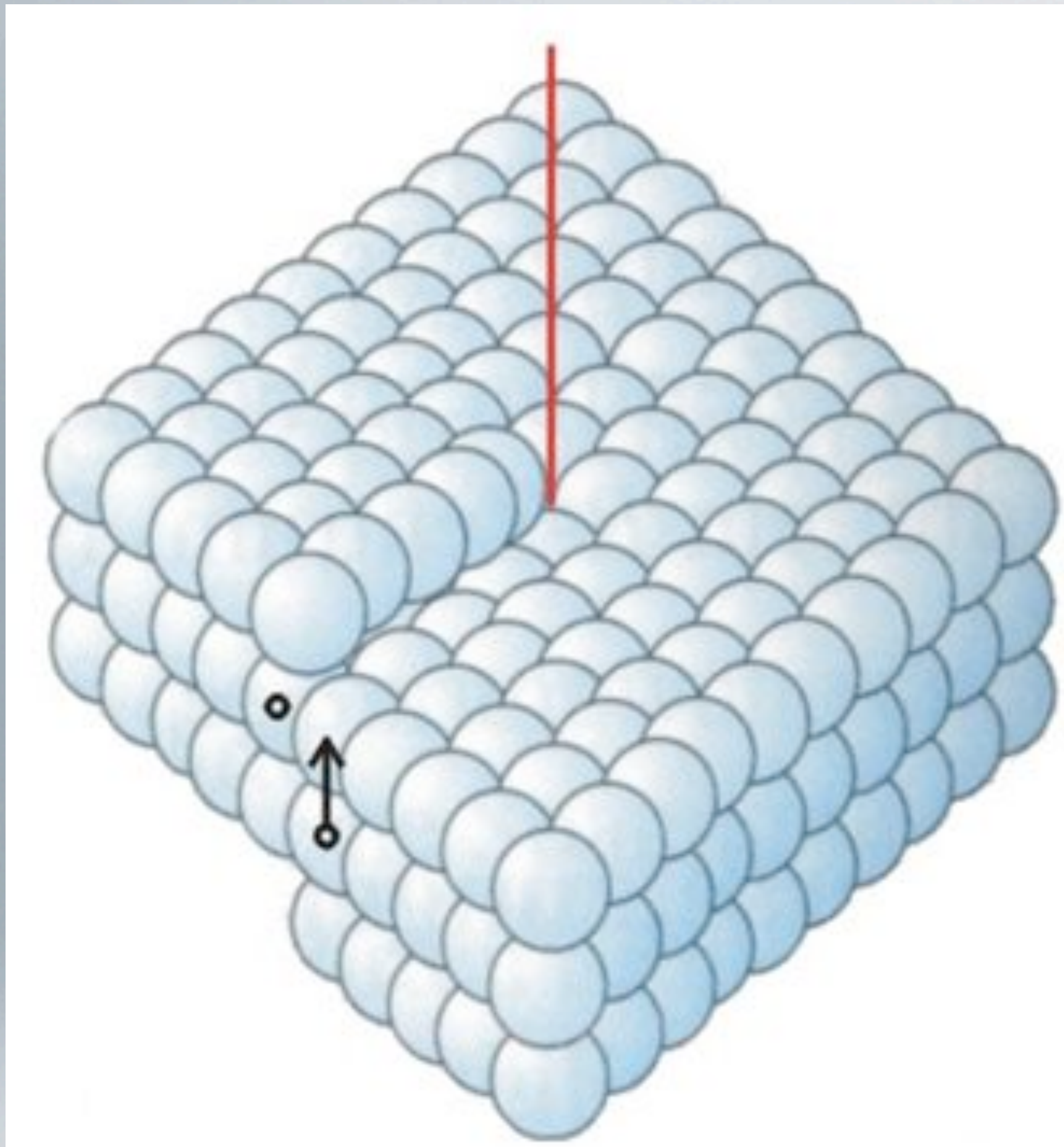
Assuming $\frac{a^2\sigma}{KT} = 5$ and S = 1,1, we got:

$$P = \exp\left[\frac{-100}{0,1}\right] = \exp\left(10^{-3}\right) = 10^{-434}$$

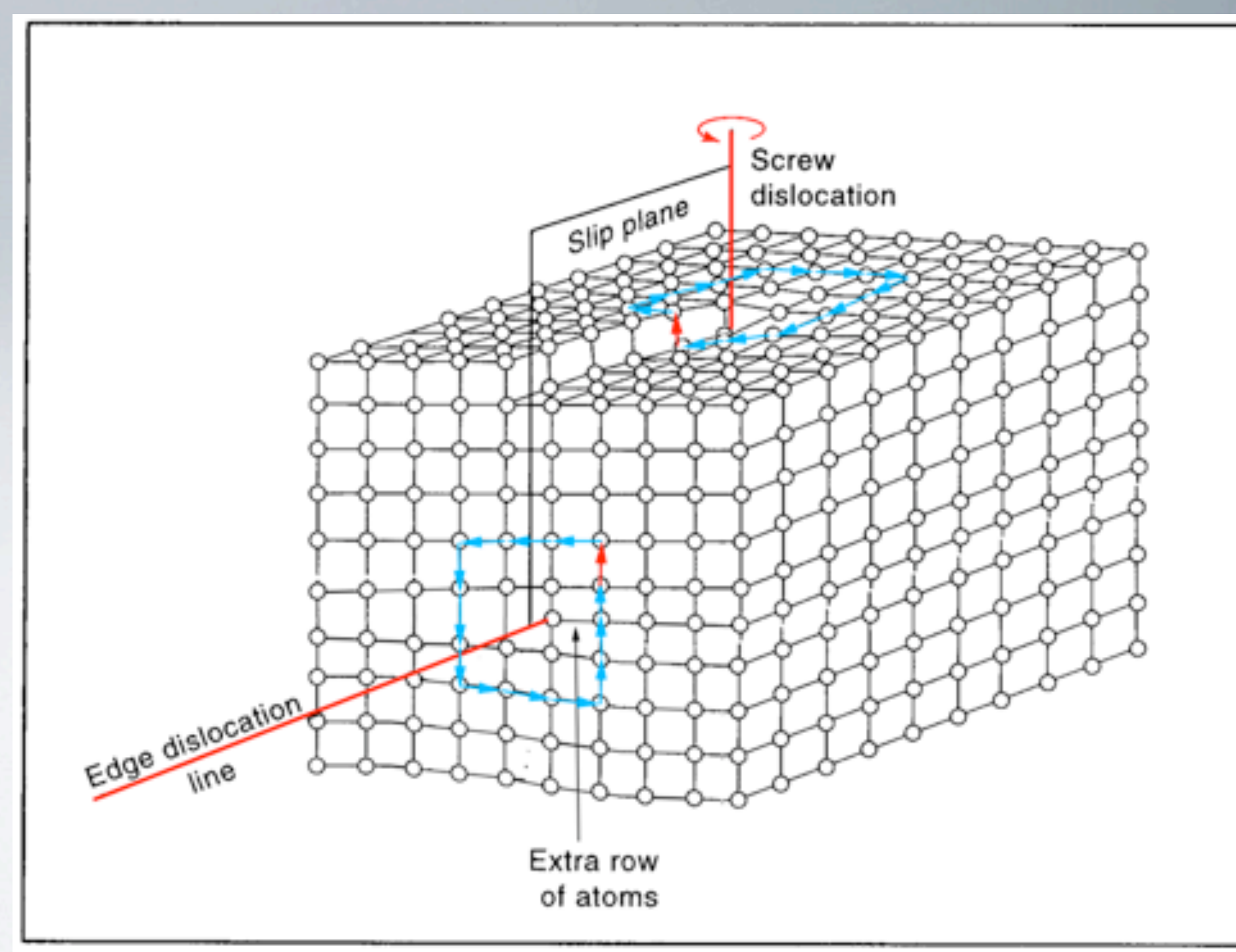
Parabolic trend with supersaturation

Crystals could no grow at a supersaturation values of 10% !!!

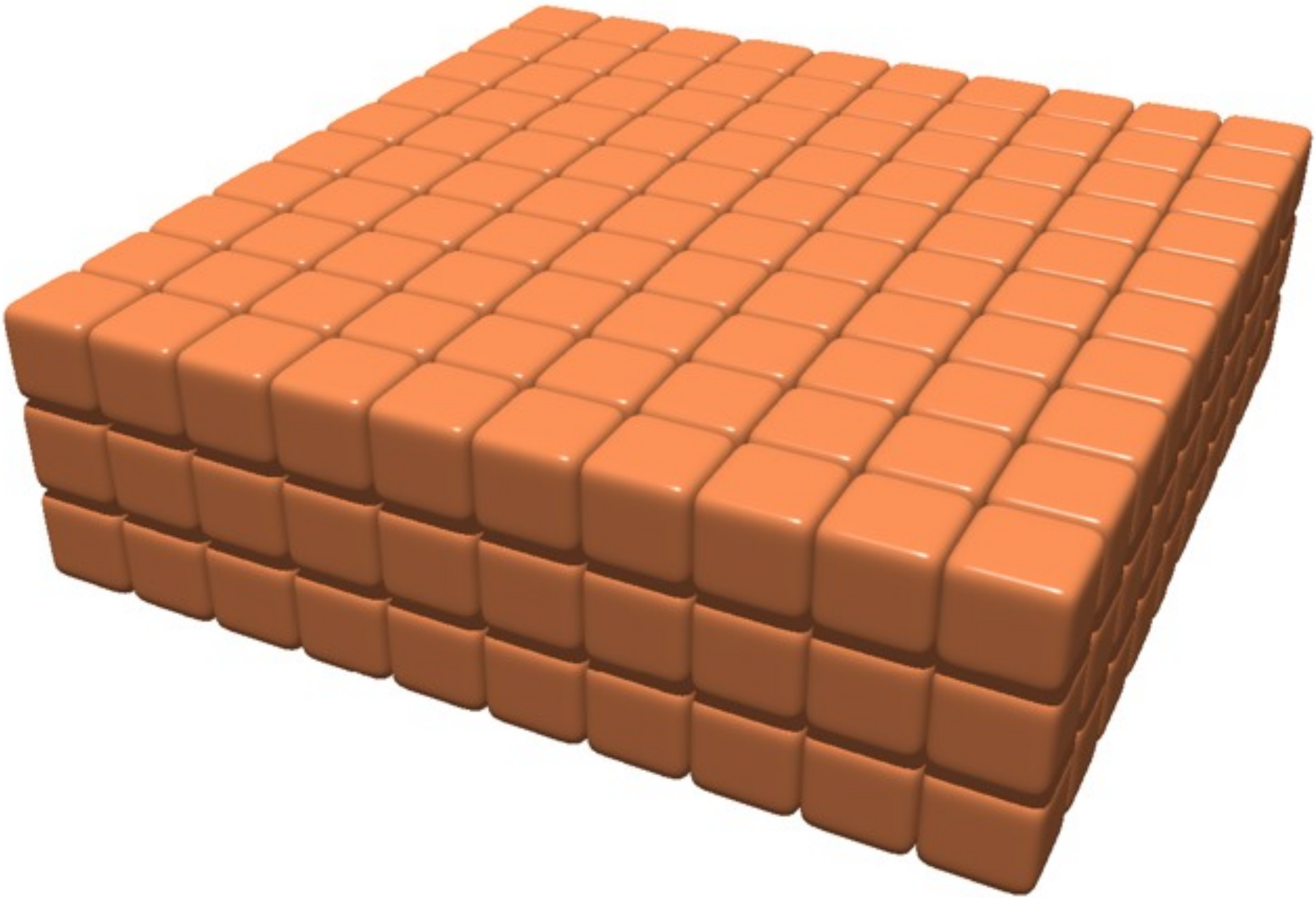
Crystal Growth Mechanisms
Screw dislocation

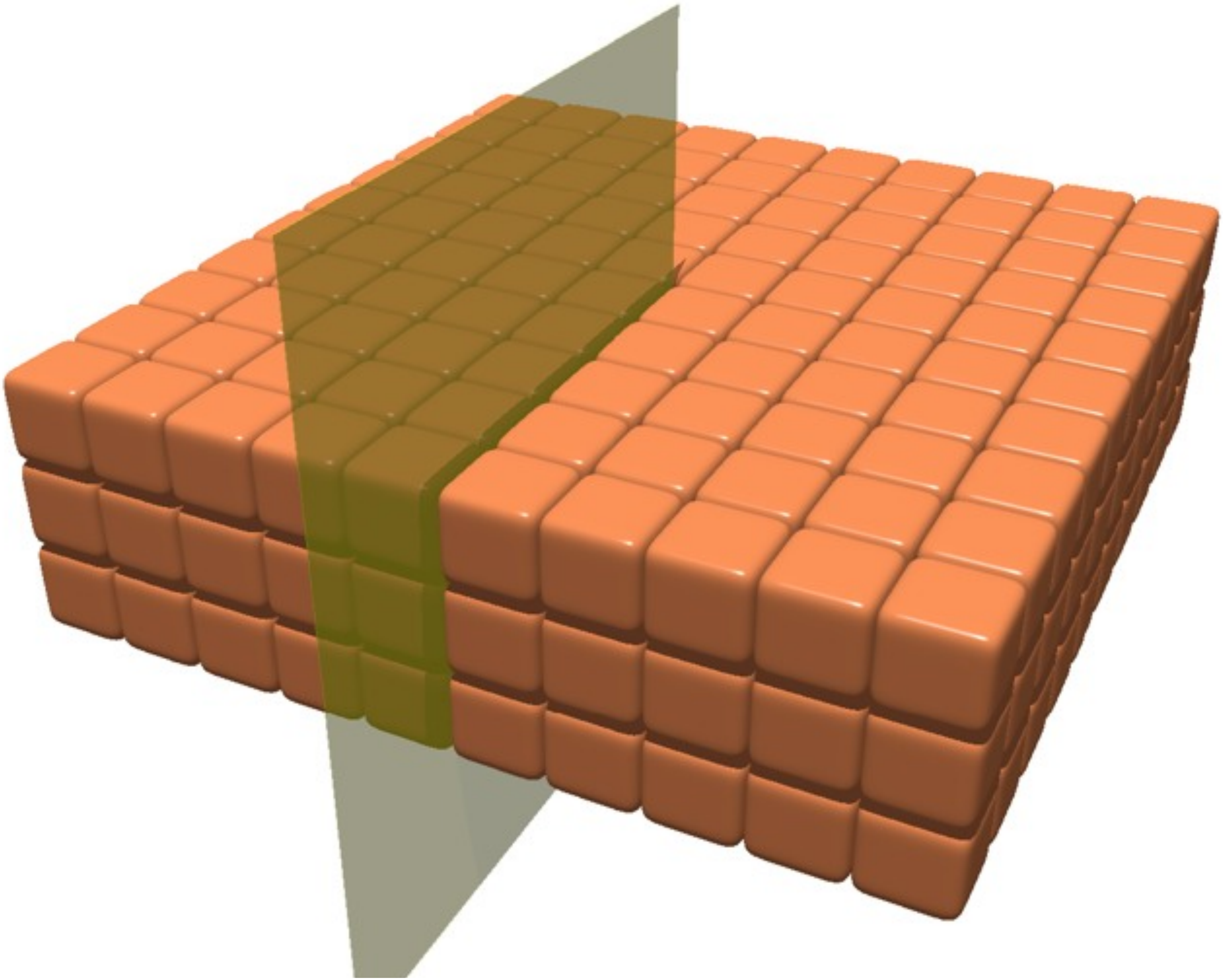


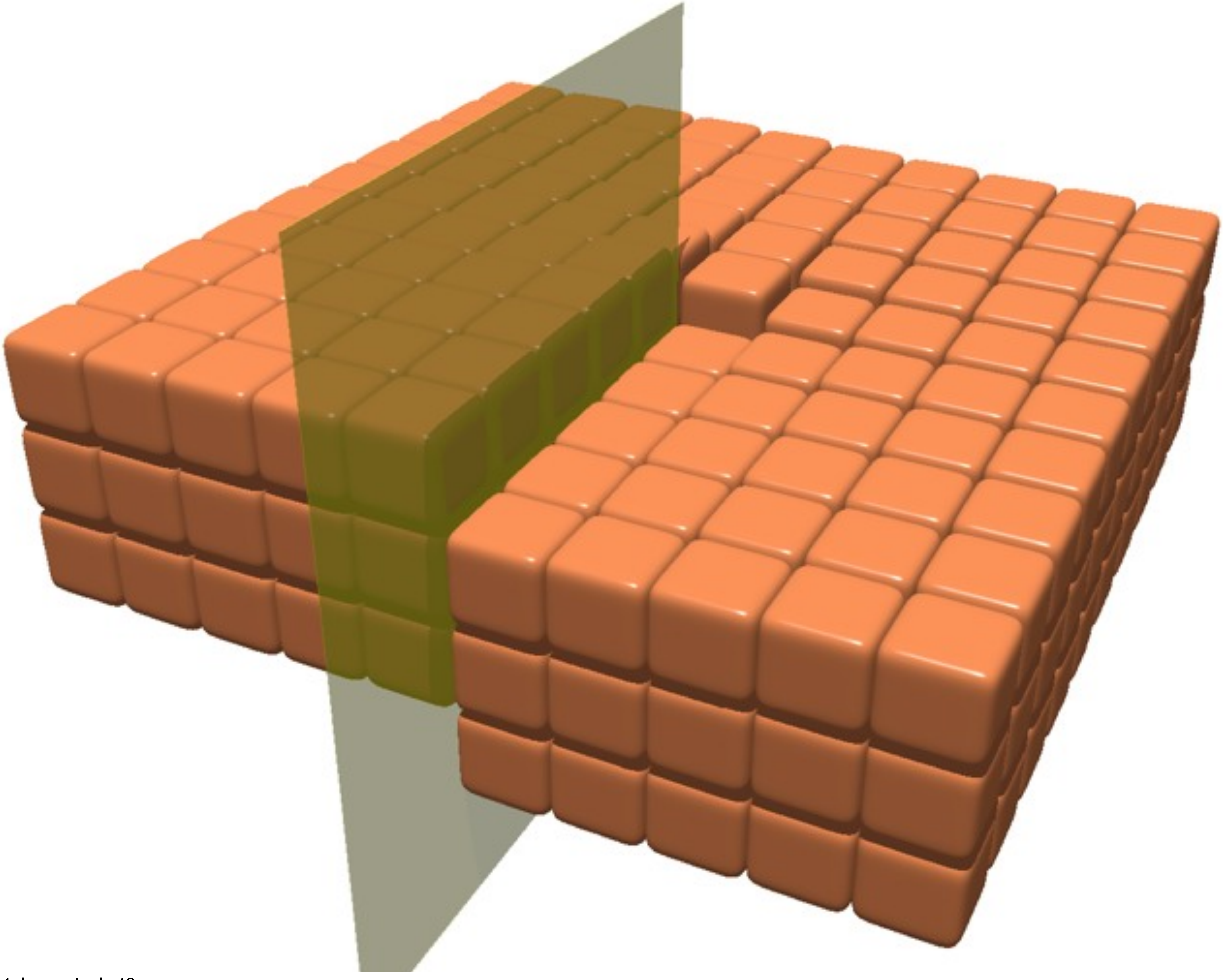
Dislocations are linear defects in the crystal structure. There are edge dislocations and screw dislocations.

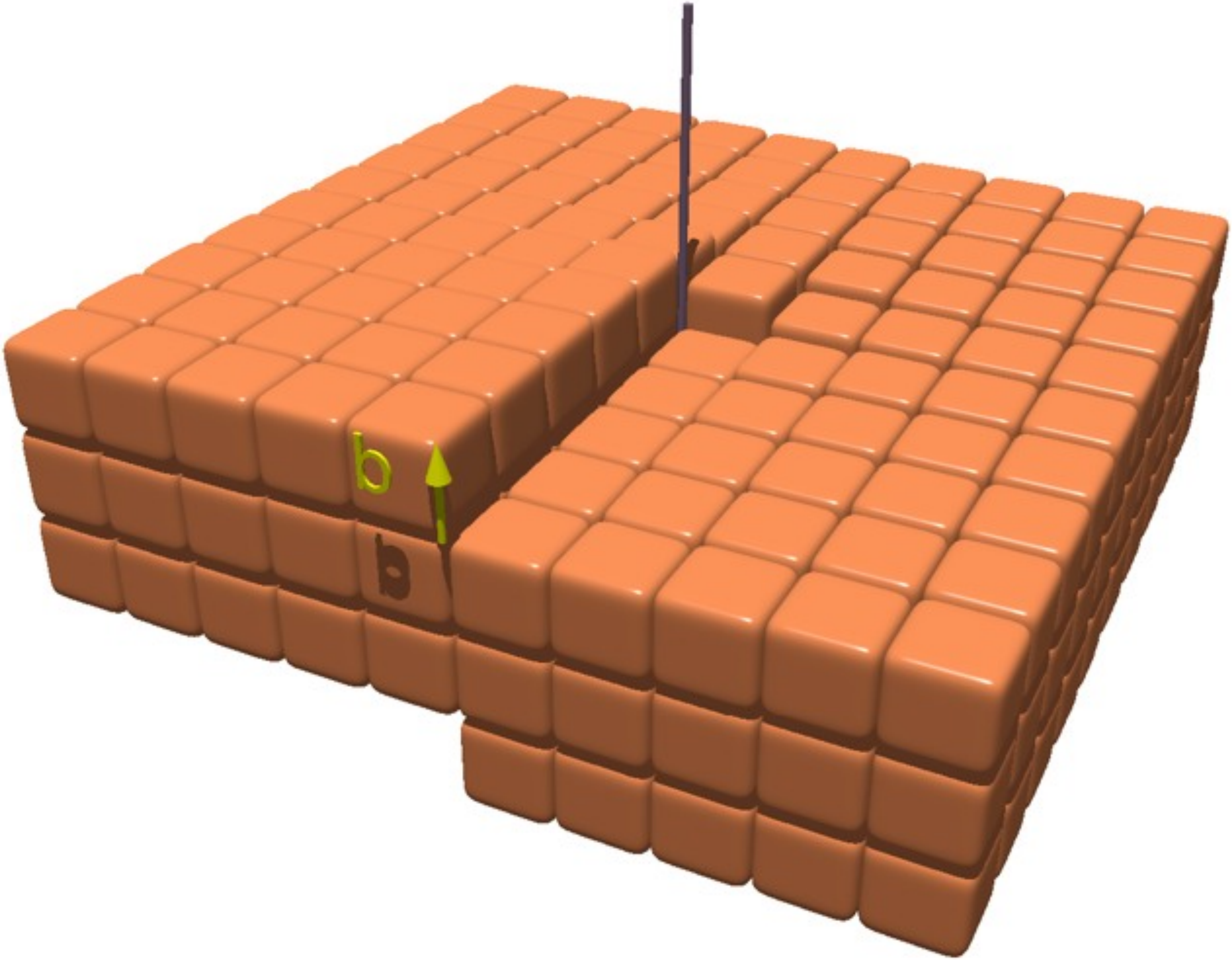


Screw Dislocations play a very important role in very growth of a crystal

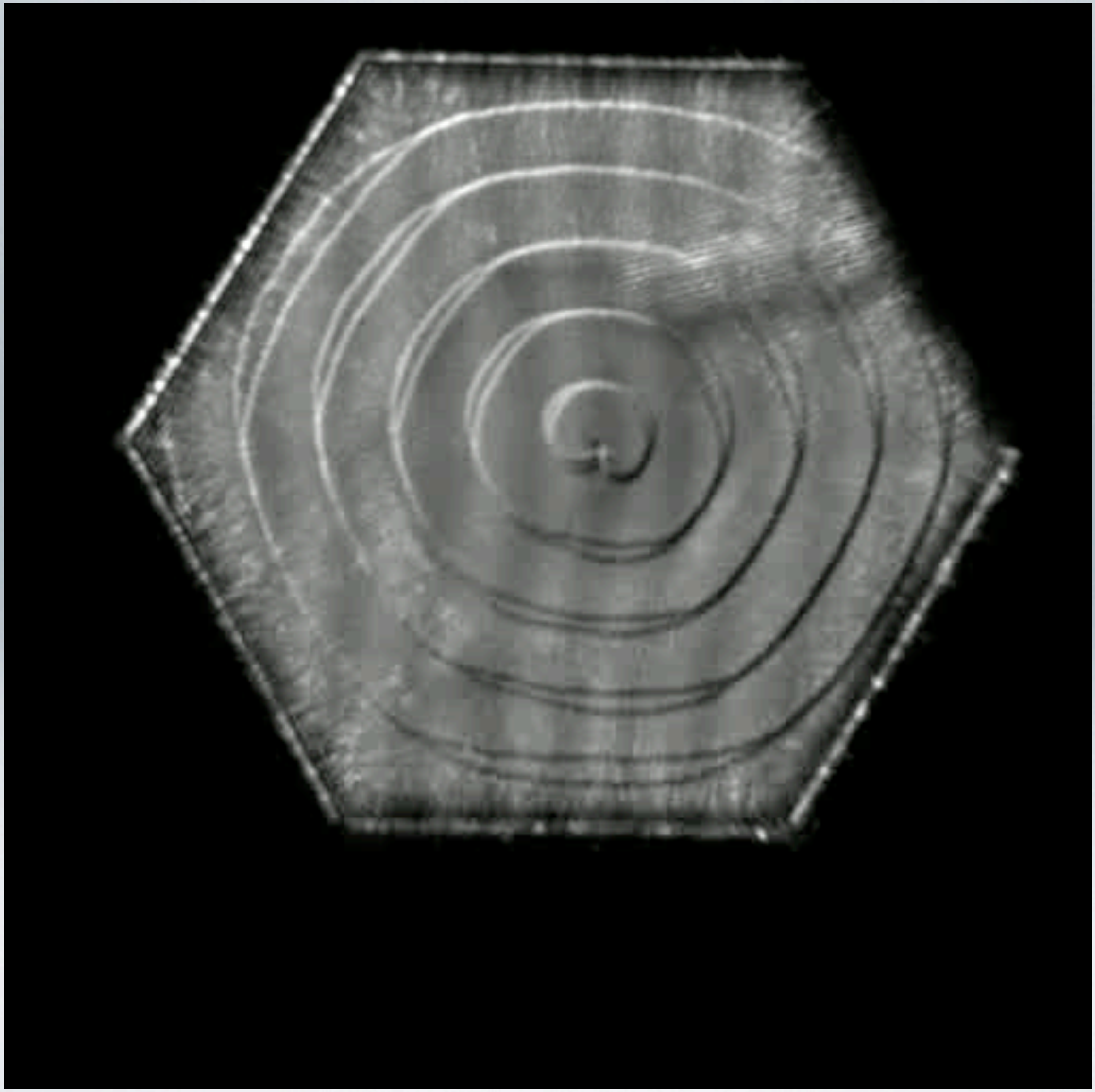




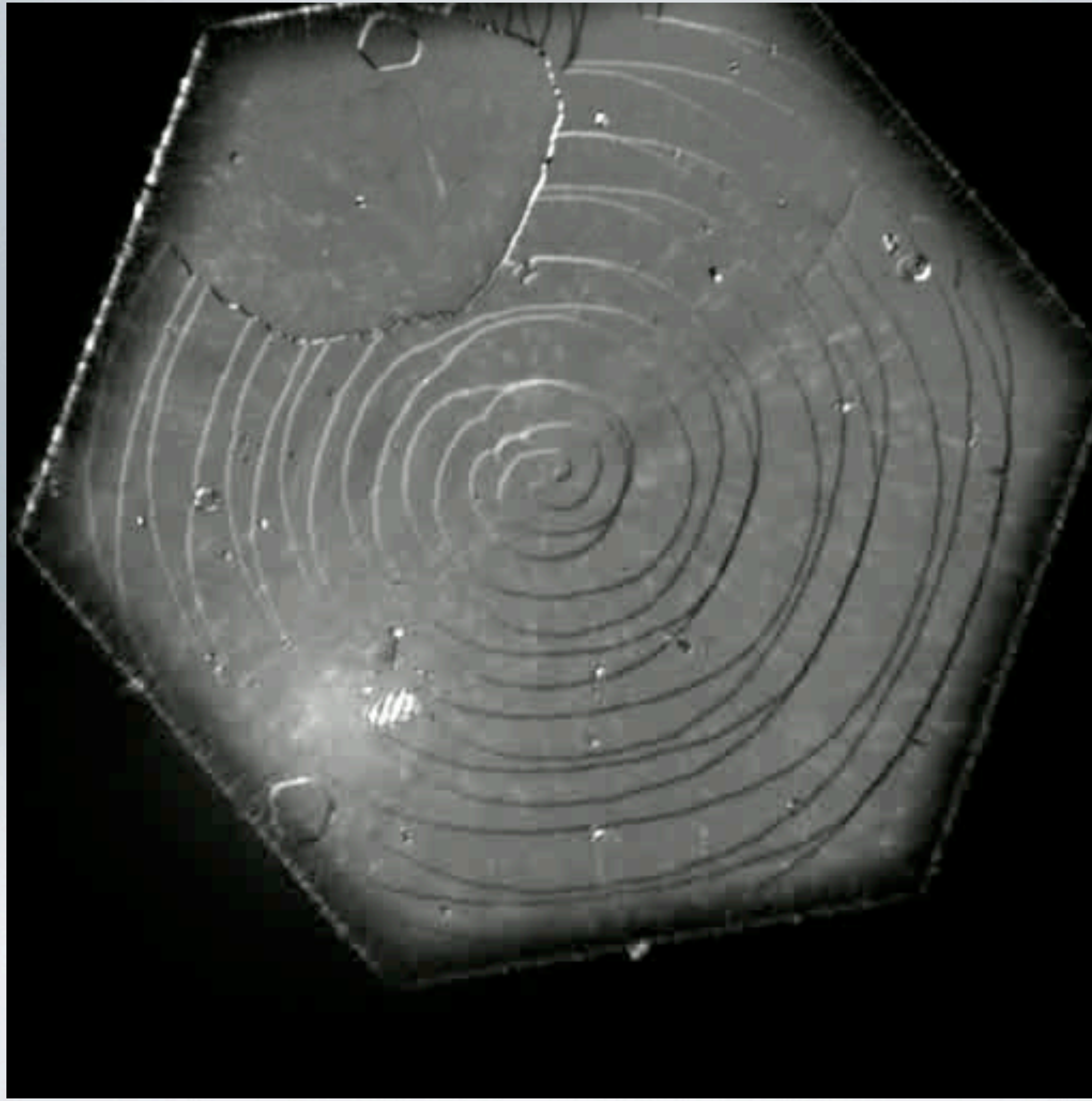



b
b

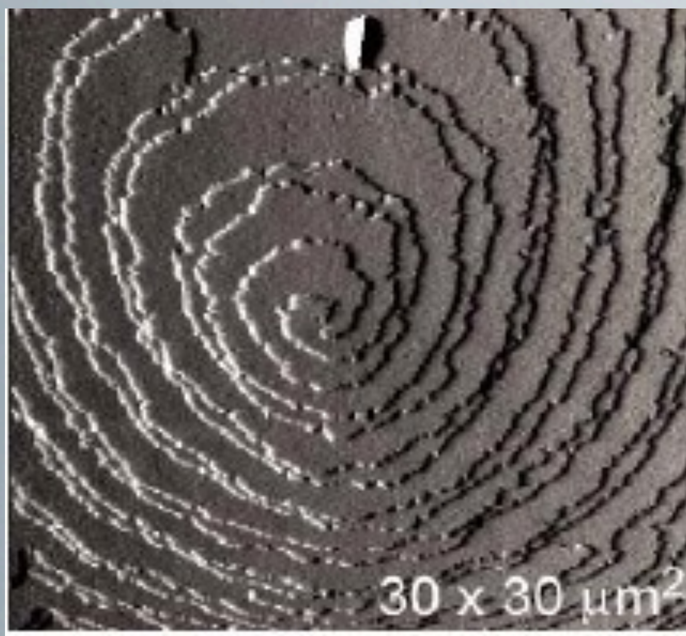
Screw dislocation growth

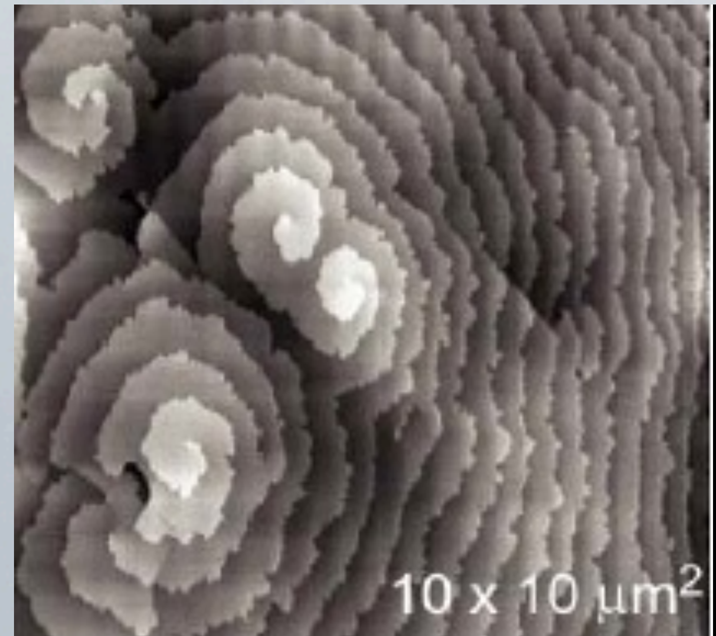


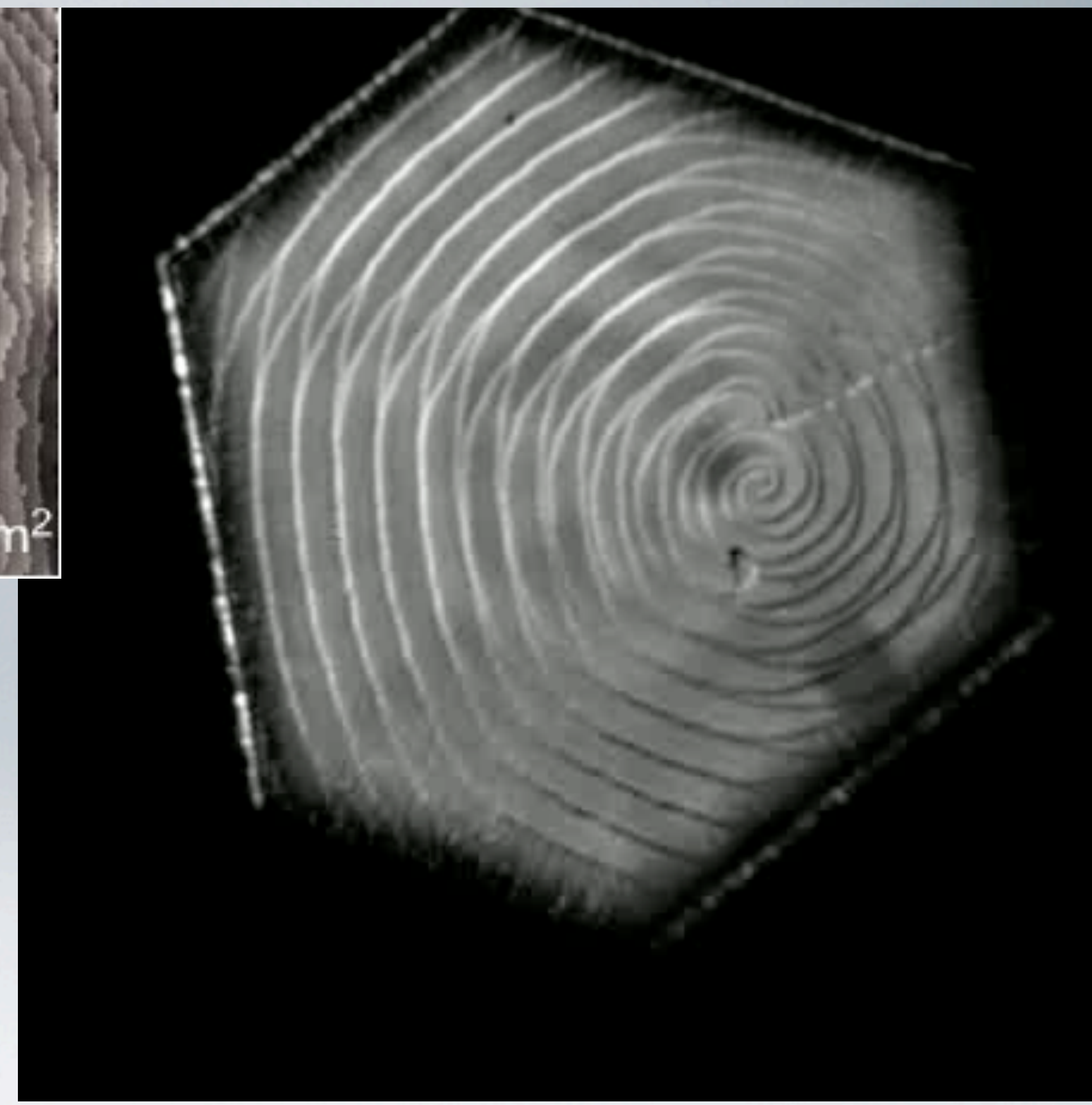
Screw dislocation growth



Screw dislocation growth







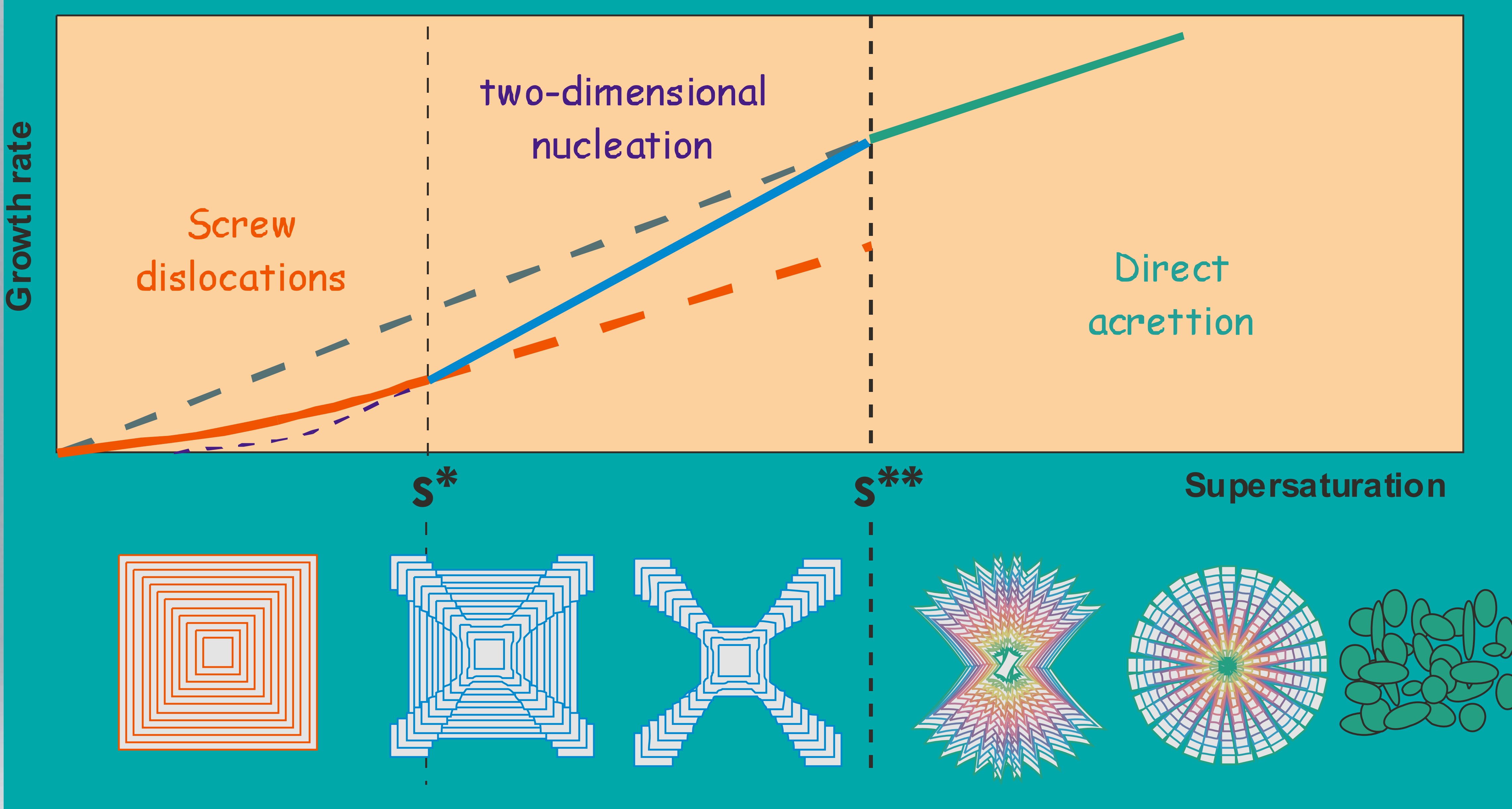
$R = k\sigma^2 \tanh \sigma^{-1}$

Alexander McPherson, Yu G. Kuznetsov, Alexander Malkin and Marco Plomp
Macromolecular Crystal Growth As Revealed By Atomic Force Microscopy

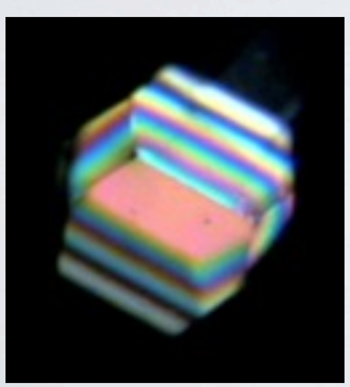
$R = k\sigma^2 \tanh \sigma^{-1}$

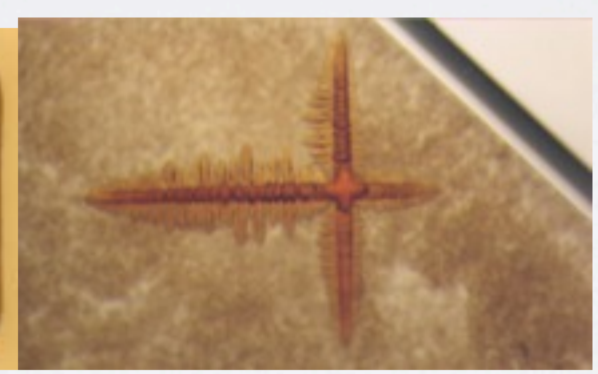
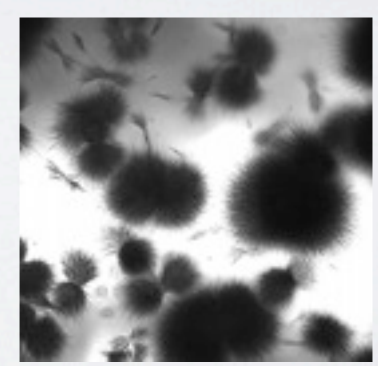
Parabolic trend at low supersaturation then linear trends

Growth mechanisms



Morphological output



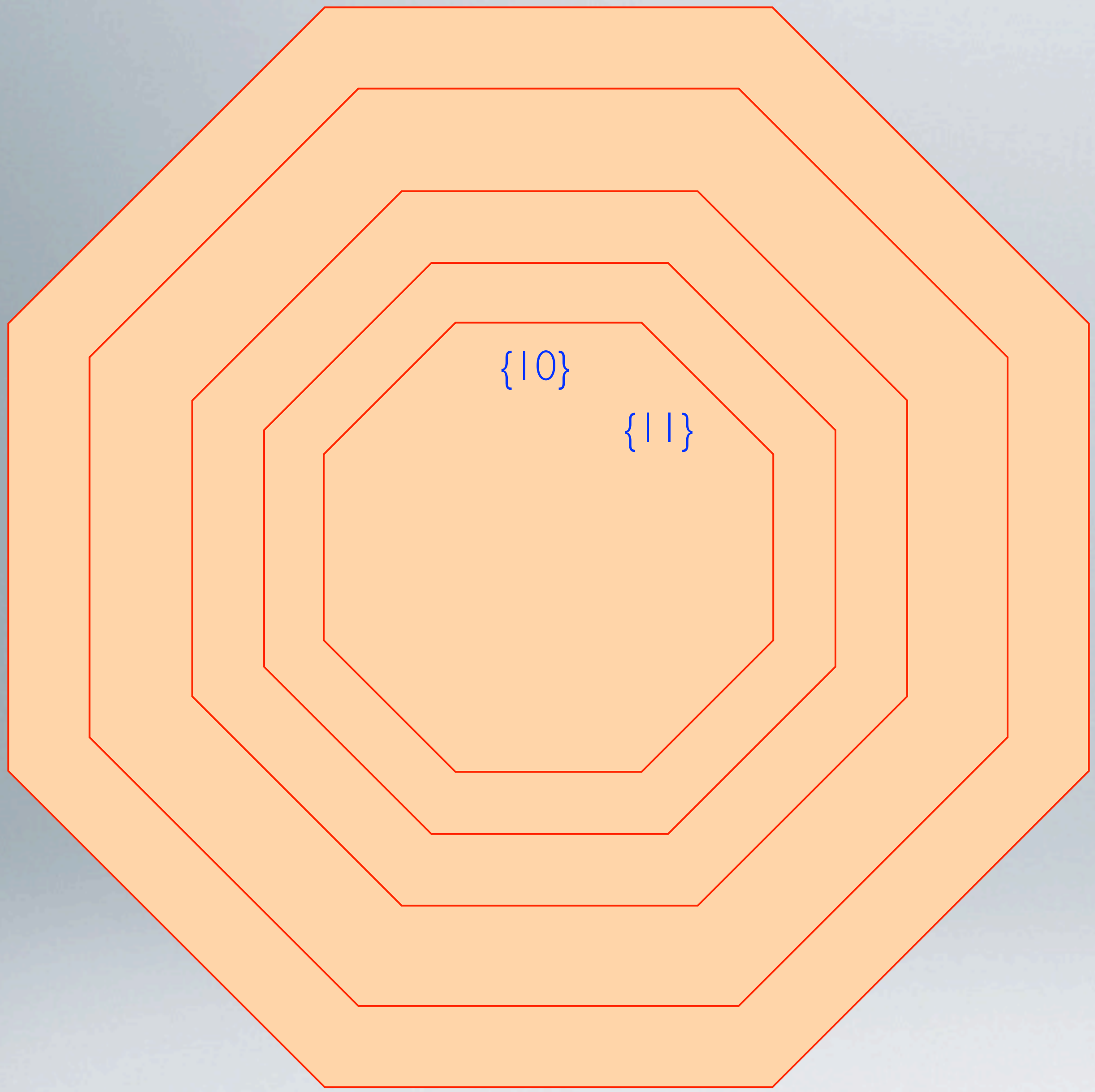
$R_{10} = R_{11}$

$R_{10} < R_{11}$

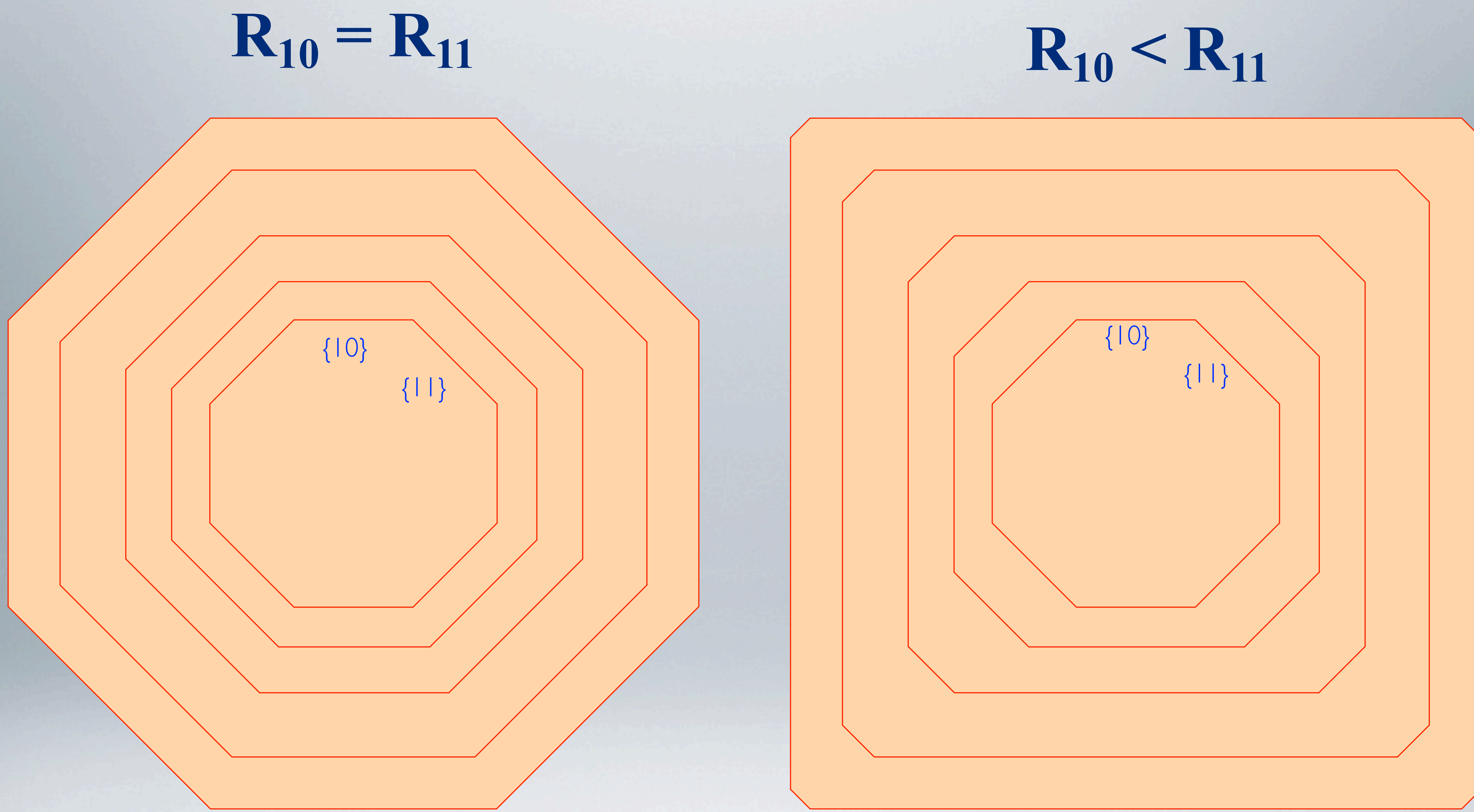
The slowest the growth rate the larger the morphological importance
At equilibrium, crystals are shaped by the faces with the slowest crystal growth rates

$R_{10} = R_{11}$

$R_{10} < R_{11}$



The slowest the growth rate the larger the morphological importance
At equilibrium, crystals are shaped by the faces with the slowest crystal growth rates



The slowest the growth rate the larger the morphological importance
At equilibrium, crystals are shaped by the faces with the slowest crystal growth rates

A Phase-Shifting Mach-Zehnder interferometry study

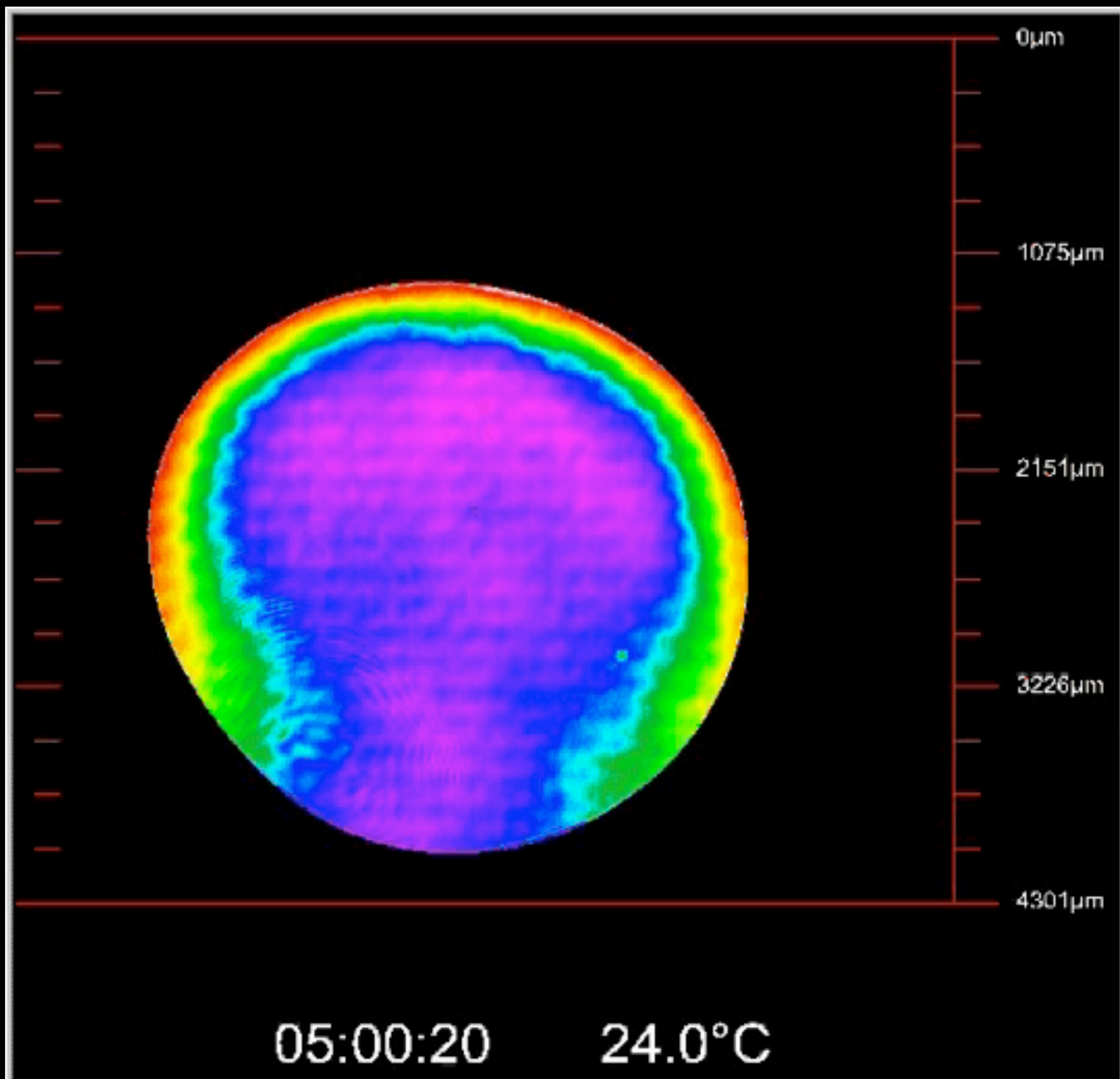
- NaCl at 4.8M, 4.4M, 4.0M in 10μL drops.
- Leave drops to evaporate until dryness.
- Follow *in situ* by PSI Mach-Zehnder Interferometry.

Supersaturation is indicated by colour code

- Density of water (0.998 g/cm^3)
- Diameter of the drop (3.0 mm)
- **Viscosity of water (1002 Pa.s)**
- **Average velocity: 0.014 mm/s**

Re = 0,40

Laminar flow: parallel layers, with no disruption between them.



- NaCl at 4.8M, 4.4M, 4.0M in 10µL drops.
- Leave drops to evaporate until dryness.
- Follow *in situ* by PSI Mach-Zehnder Interferometry.

Supersaturation is indicated by colour code

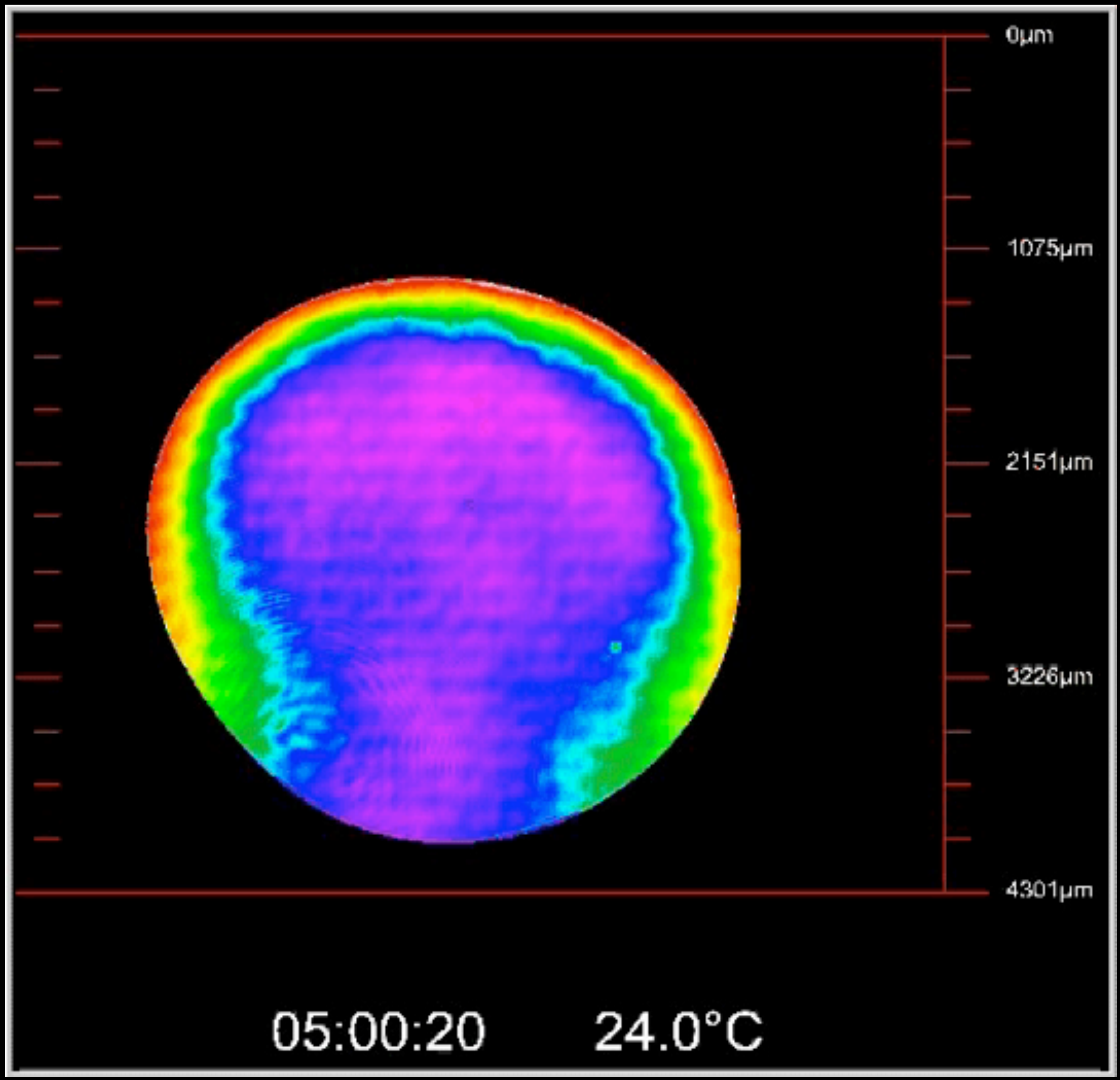
- Density of water (0.998 g/cm^3)
- Diameter of the drop (3.0 mm)
- **Viscosity of water (1002 Pa.s)**
- **Average velocity: 0.014 mm/s**

Re = 0,40

Laminar flow: parallel layers, with no disruption between them.

Dynamics of a crystalizing drop
A demonstration of the role of gravity

A Phase-Shifting Mach-Zehnder interferometry study



- NaCl at 4.8M, 4.4M, 4.0M in 10µL drops.
- Leave drops to evaporate until dryness.
- Follow *in situ* by PSI Mach-Zehnder Interferometry.

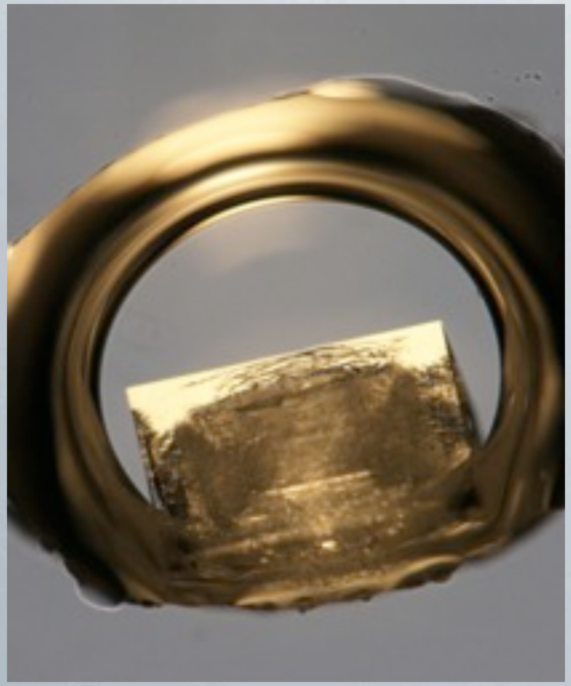
Supersaturation is indicated by colour code

- Density of water (0.998 g/cm^3)
- Diameter of the drop (3.0 mm)
- **Viscosity of water (1002 Pa.s)**
- **Average velocity: 0.014 mm/s**

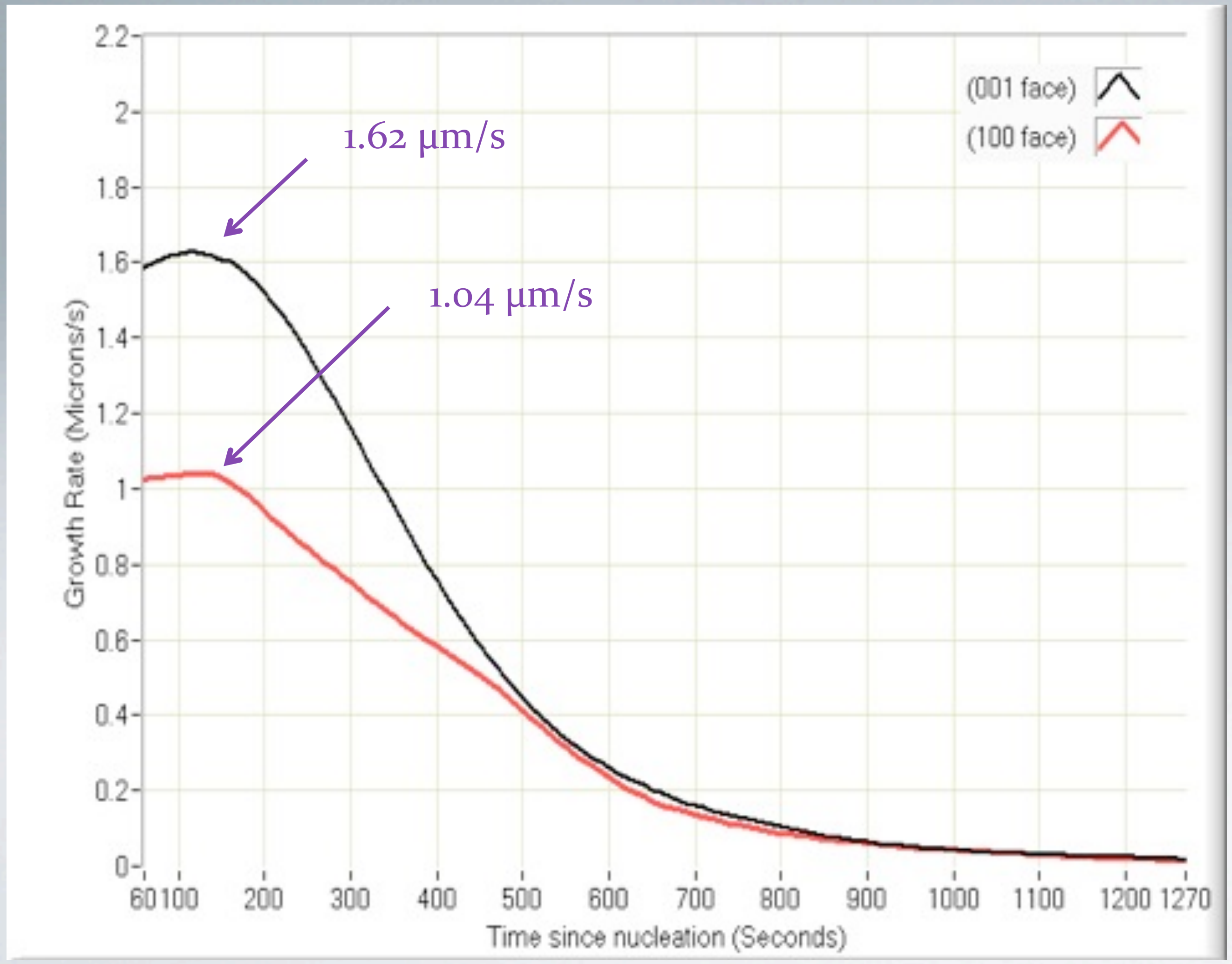
Re = 0,40

Laser beam direction
Pathlenght (1.0 mm).

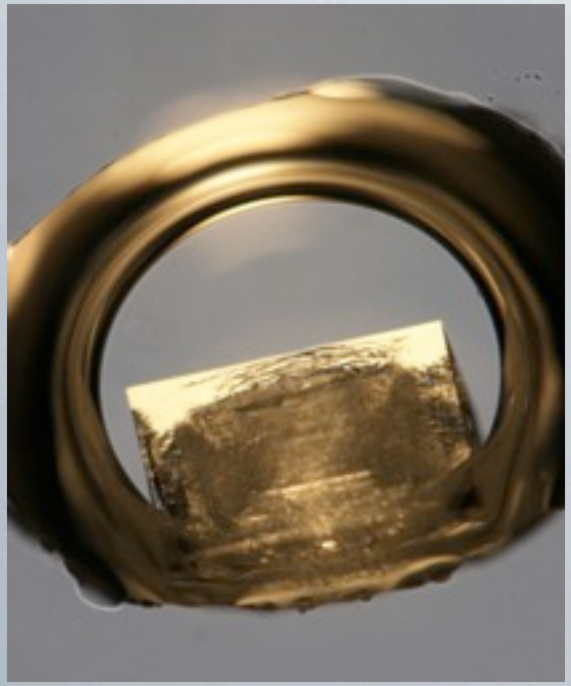
Laminar flow: parallel layers, with no disruption between them.



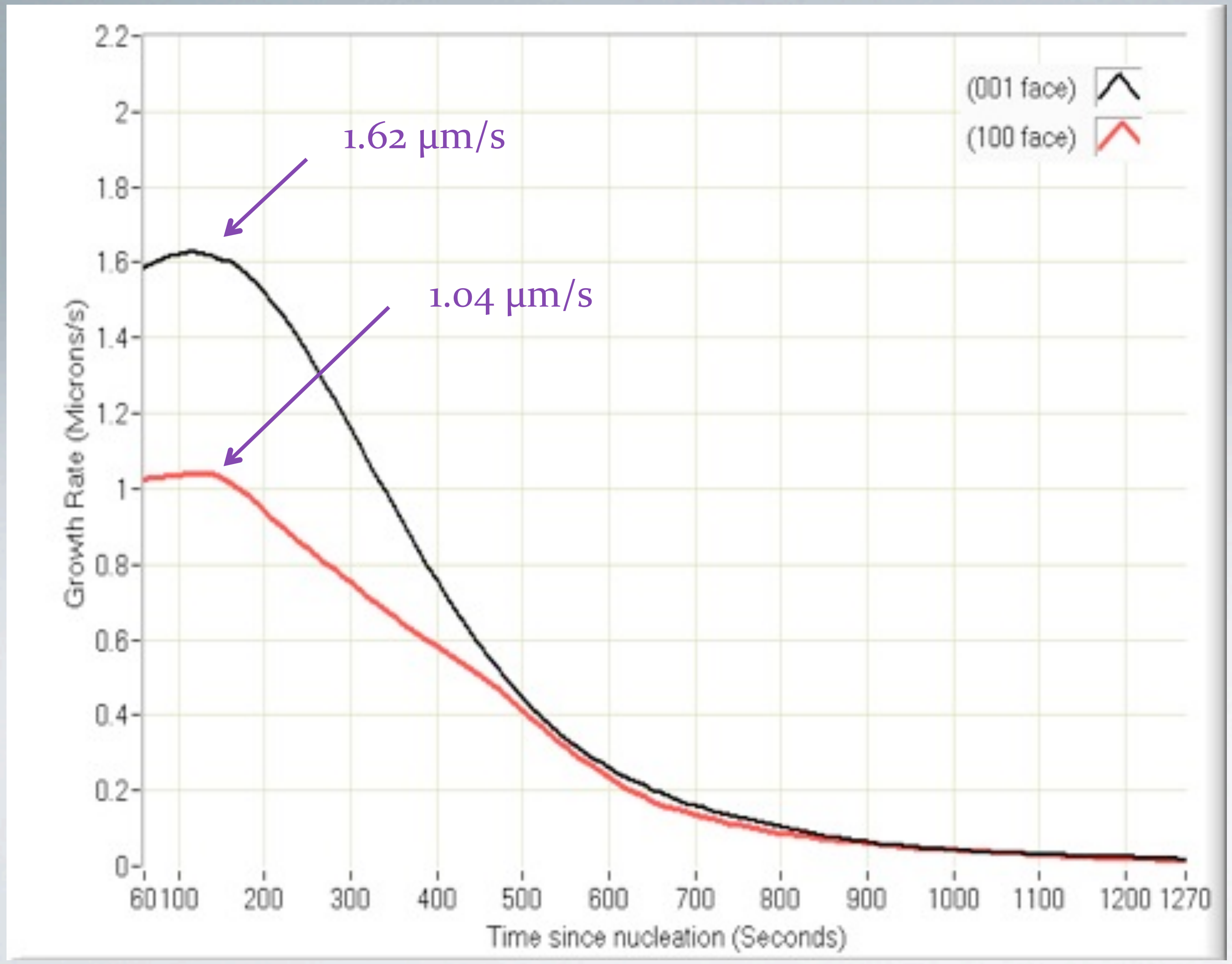
Initial concentration: 4.0 M



Mean growth rate (8 min.)	
Top face	Lateral faces
0.83 μm/s	1.14 μm/s

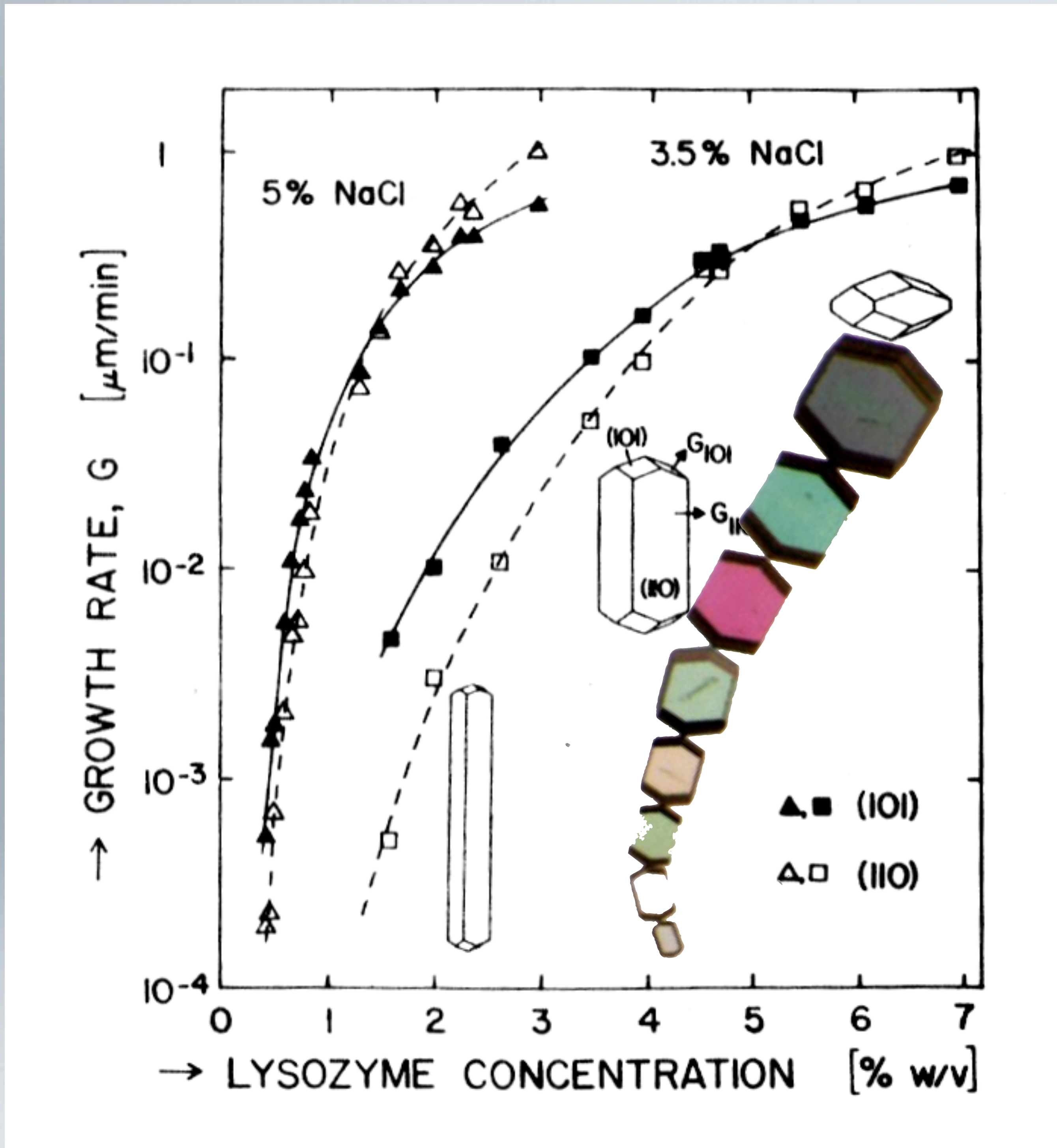


Initial concentration: 4.0 M

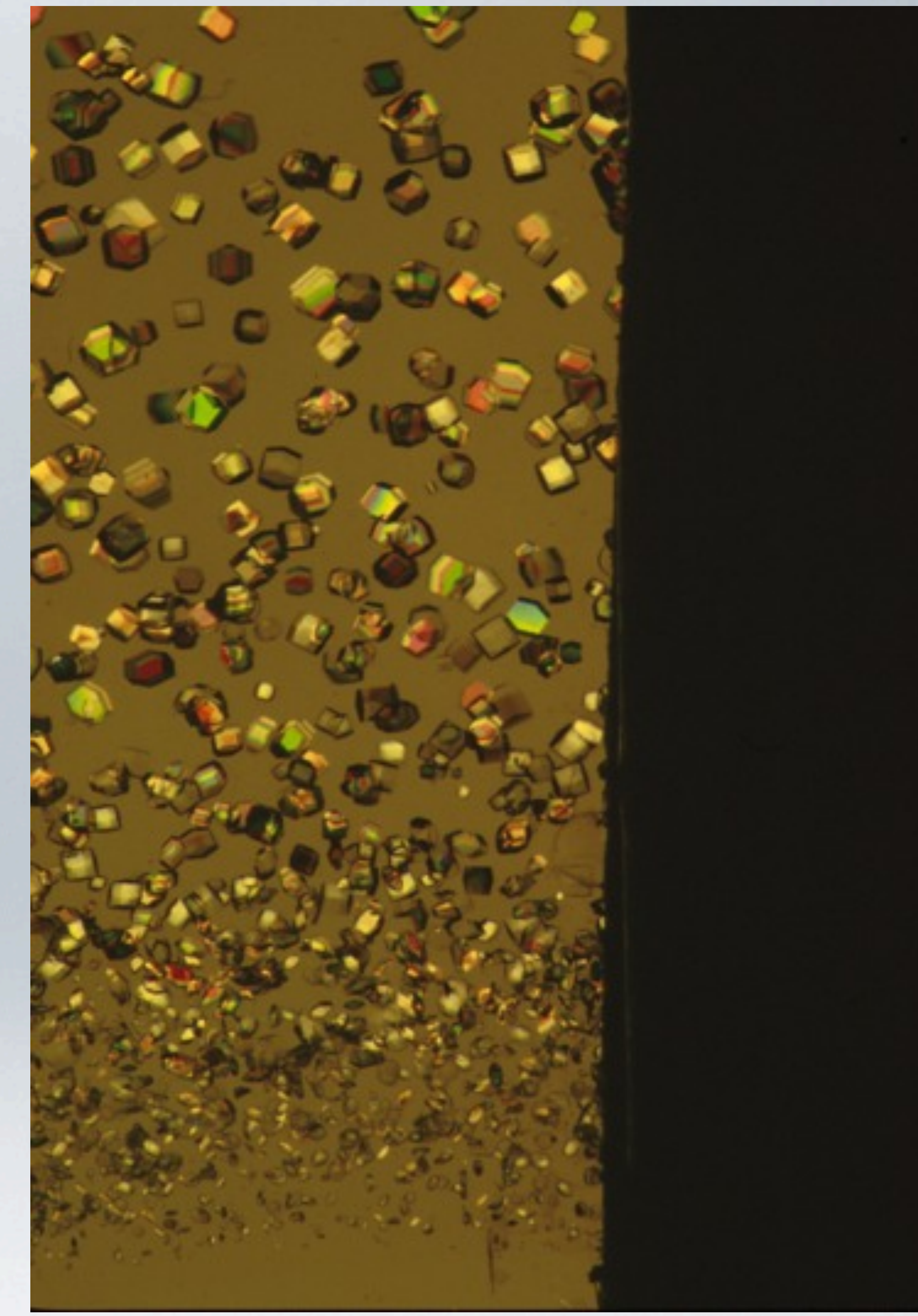


Mean growth rate (8 min.)	
Top face	Lateral faces
0.83 µm/s	1.14 µm/s

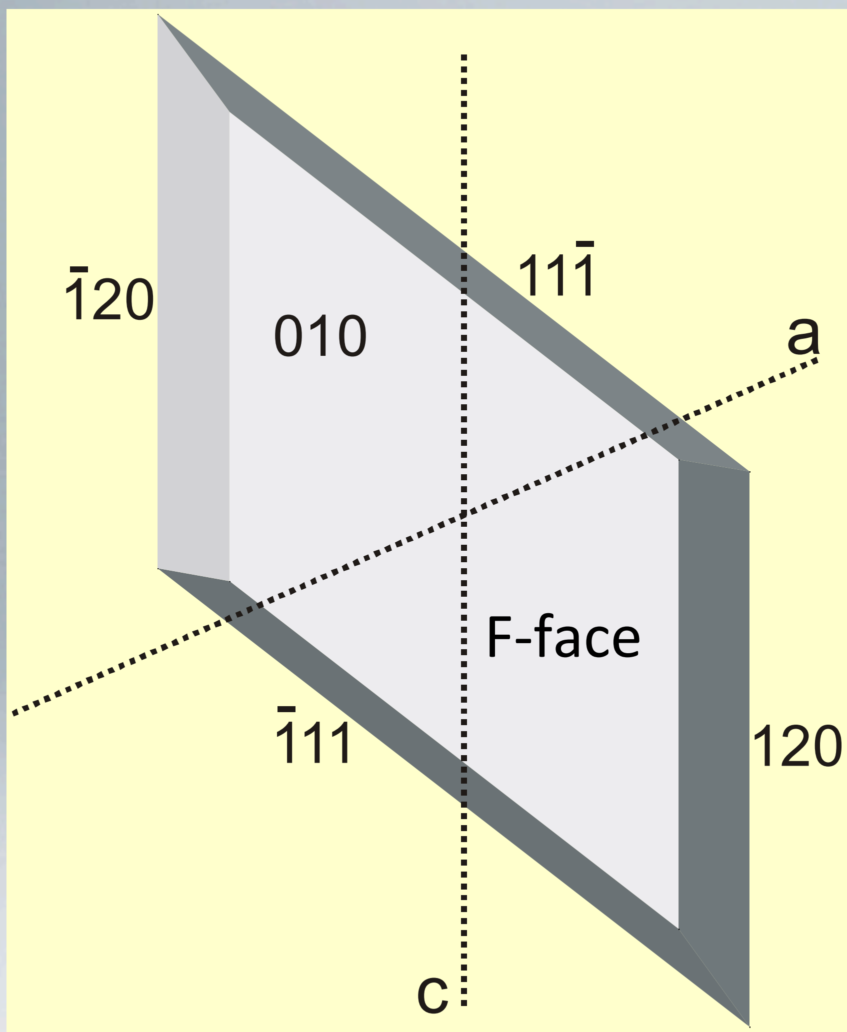
Convection greatly increases the rate of solute transport to the growth interface.

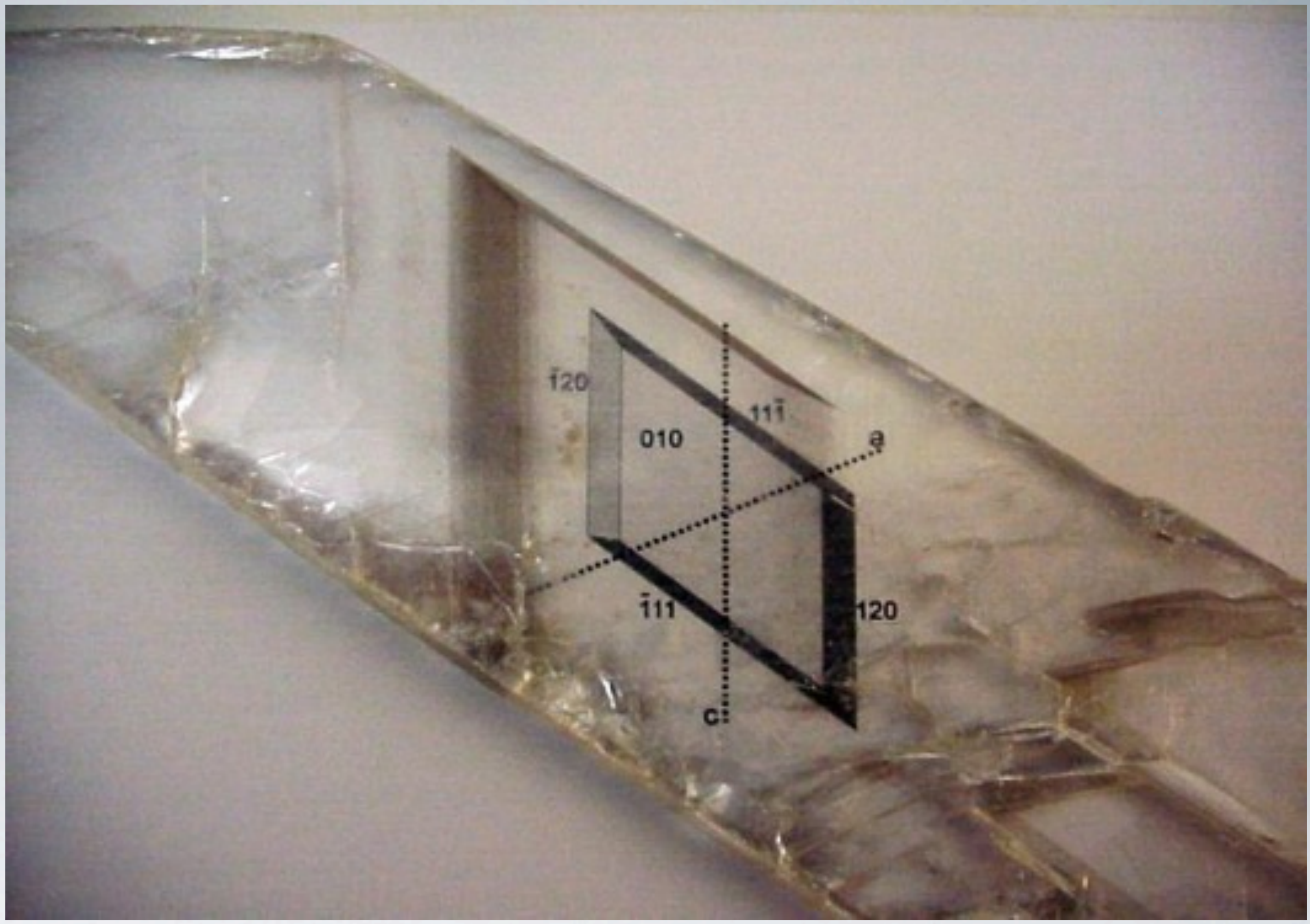


Durbin, S.D. y Feher, G., *J. Cryst. Growth*, 76 (1986) 583



The morphology of gypsum





Naica giant crystals of gypsum have grown near equilibrium

The crystal beams

The blocky crystals

Top view of a crystal beam showing the terminal faces {-111}: Notice that the large development of the prism {1k0} and the very small pinacoidal {010} faces.

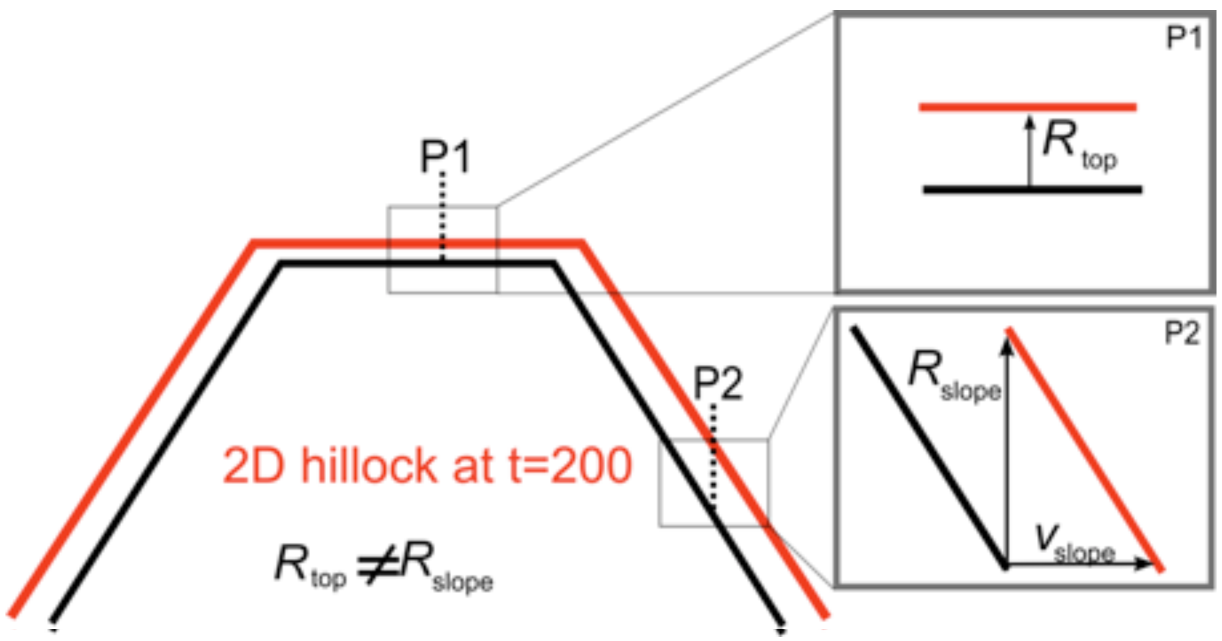
Juan Manuel García-Ruiz (CSIC-Universidad de Granada) Academia de Ciencias, Madrid, 9 de abril de 2011

Growth rate measurement | 55 °C

At 50 ºC neither growth nor dissolution could be detected

At 55 °C two growth rates:

- “fast” growth for the slope (10^{-4}nm/s)
- “slow” growth for the top (10^{-5}nm/s)



At 55 °C the growth rate is ≈10^{-5} nm/s

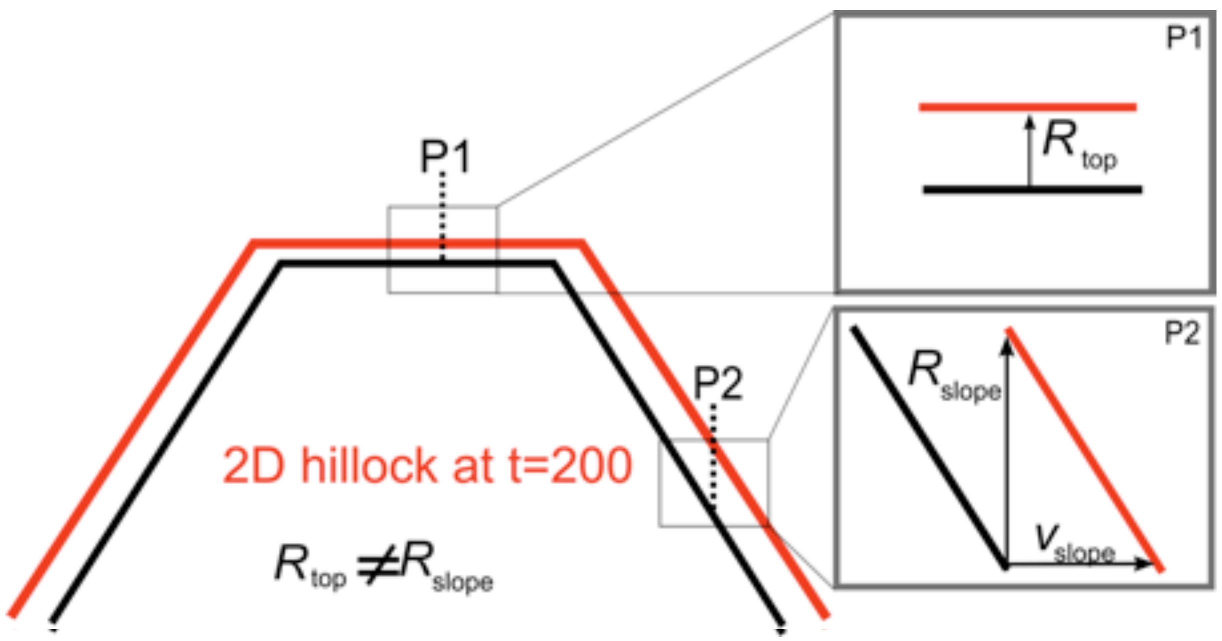
Van Driessche et al., 108 (2011) 15721

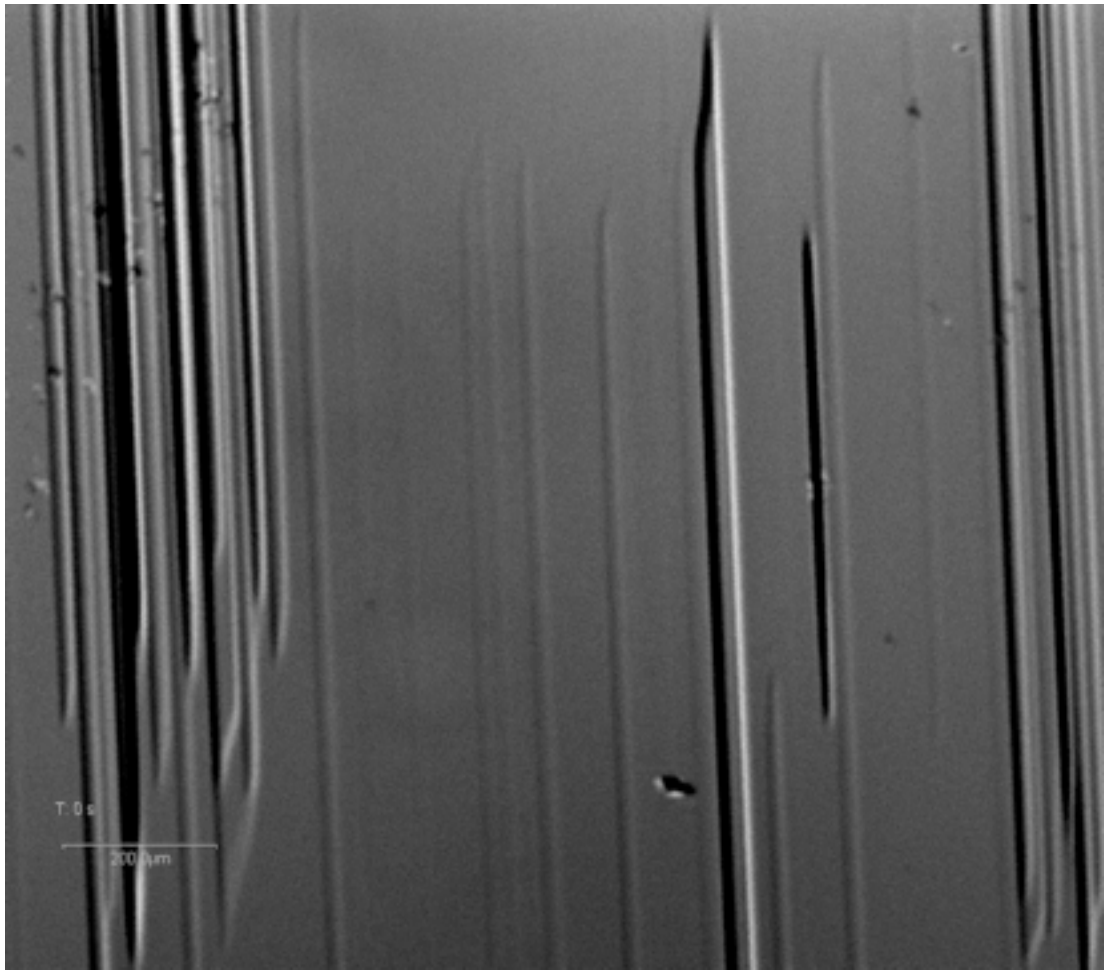
Growth rate measurement | 55 °C

- At 50 ºC neither growth nor dissolution could be detected

At 55 °C two growth rates:

- “fast” growth for the slope (10^{-4}nm/s)
- “slow” growth for the top (10^{-5}nm/s)

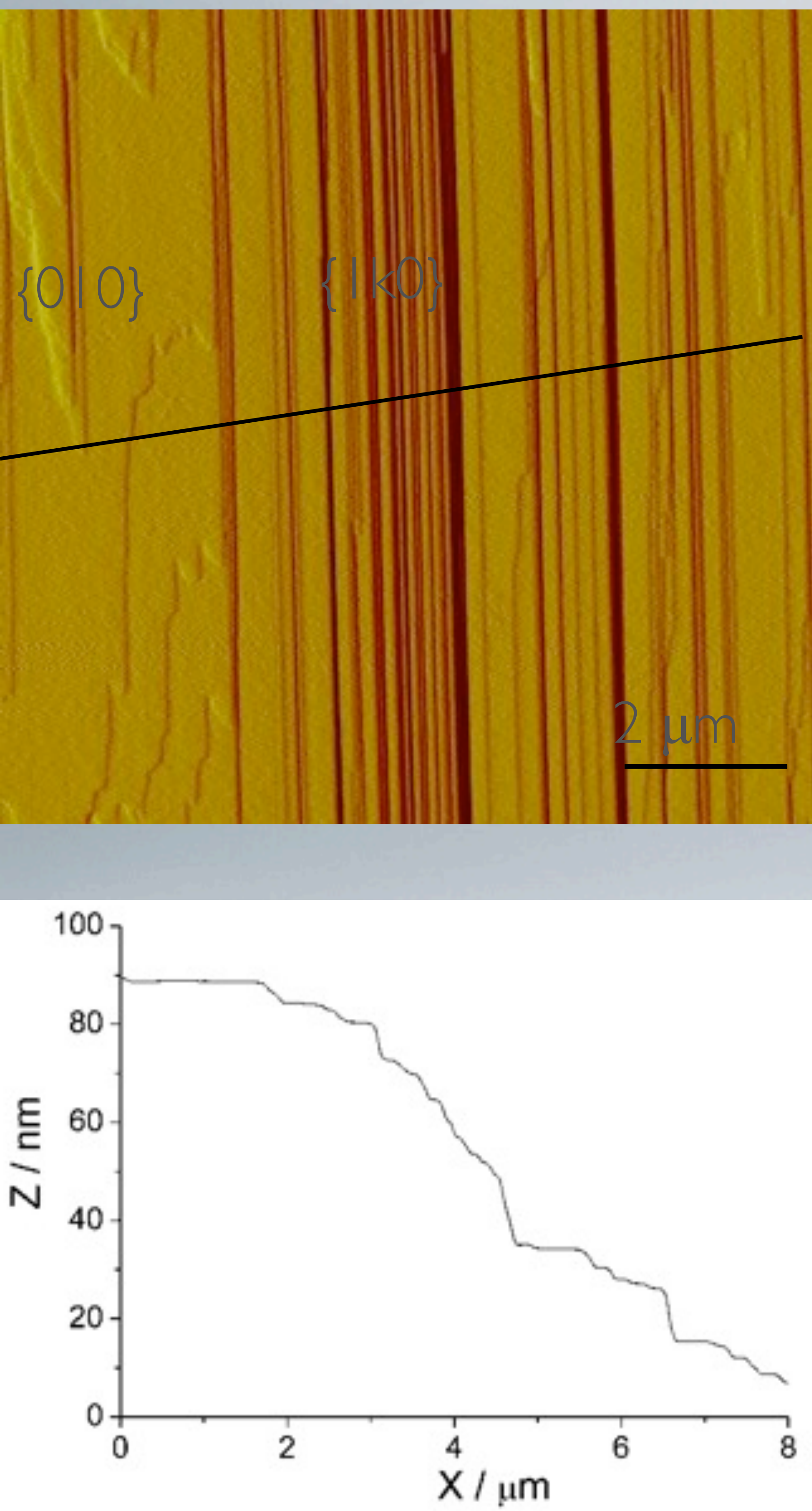




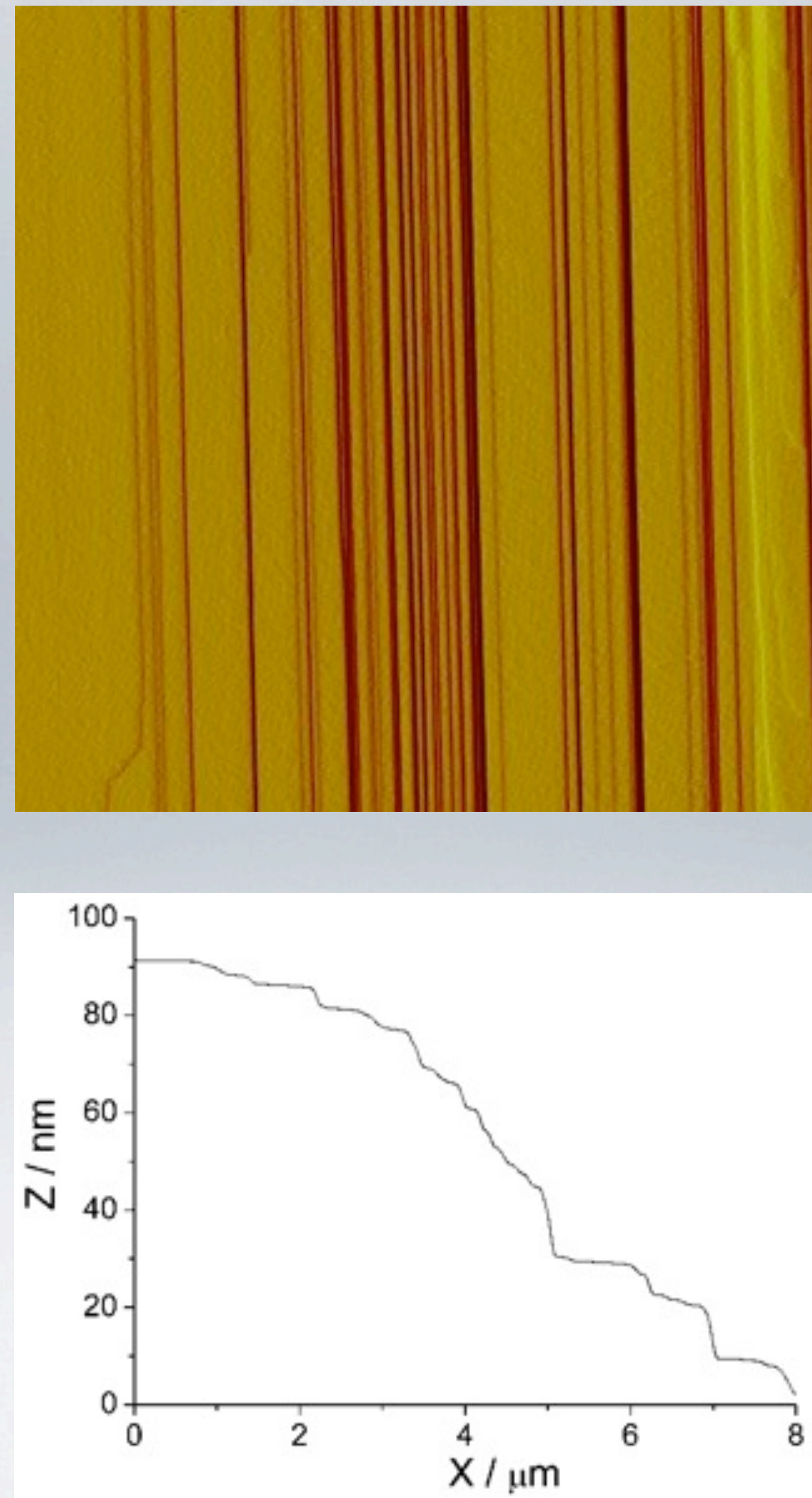
At 55 °C the growth rate is ≈10^{-5} nm/s

Van Driessche et al., 108 (2011) 15721

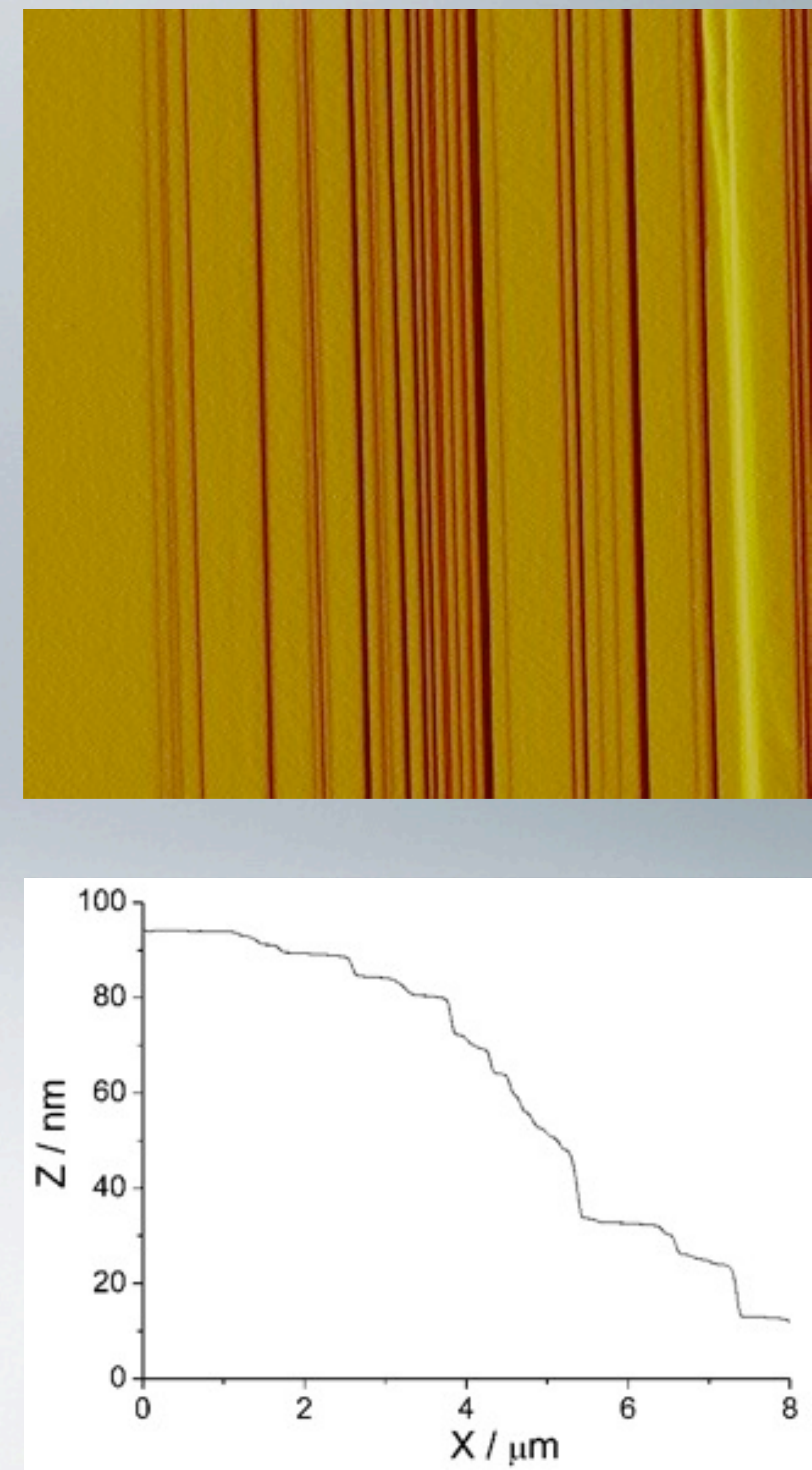
t=0



t= 33 min



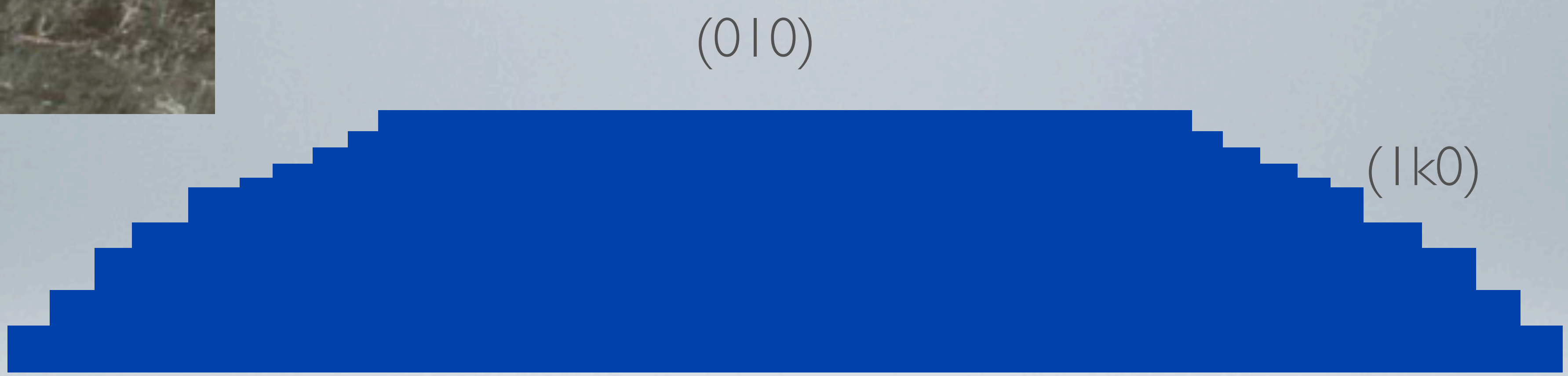
t=67 min

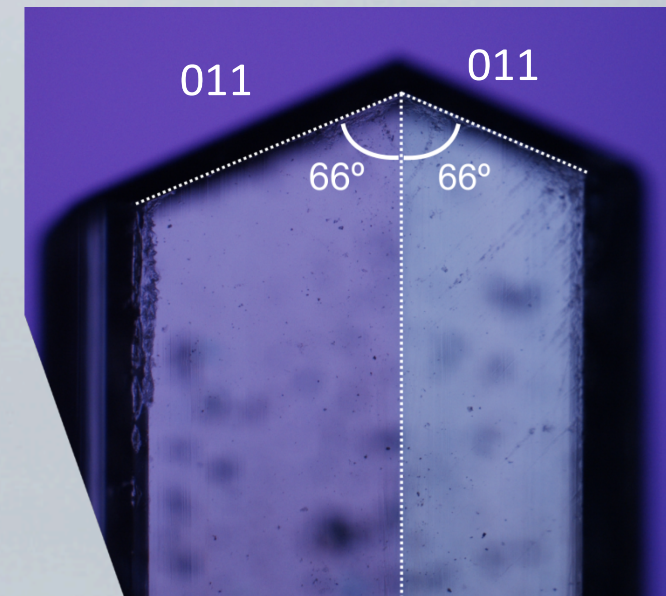


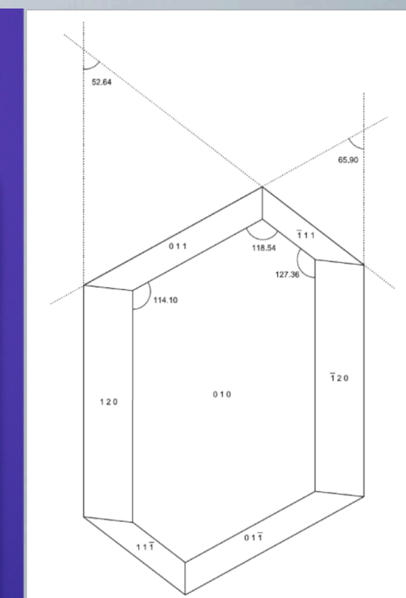

-111
010
1k0


-111
010
1k0

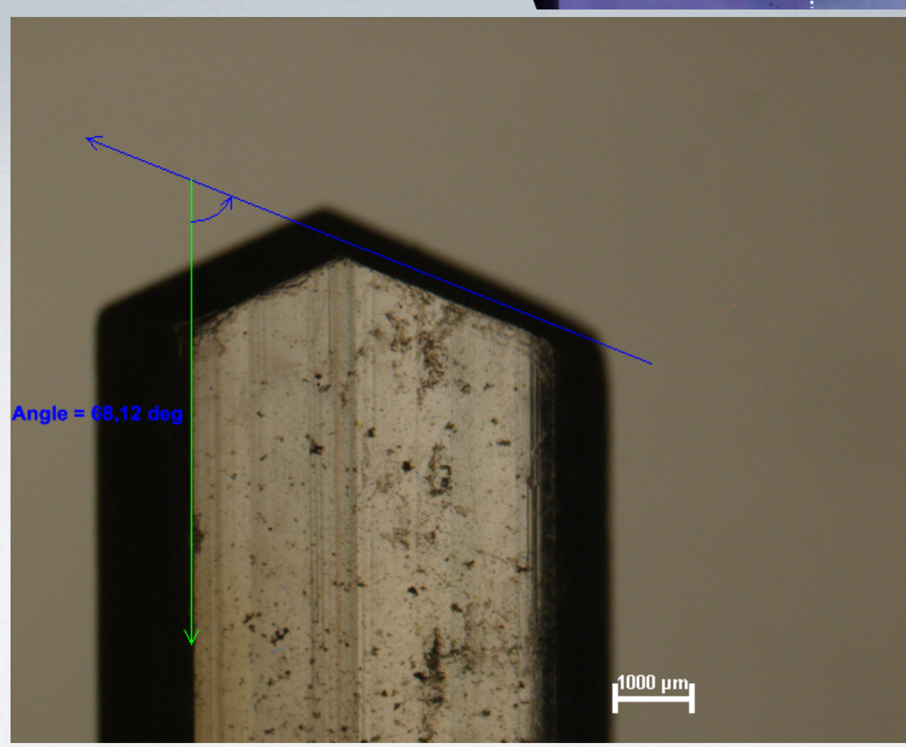

-111
010
1k0

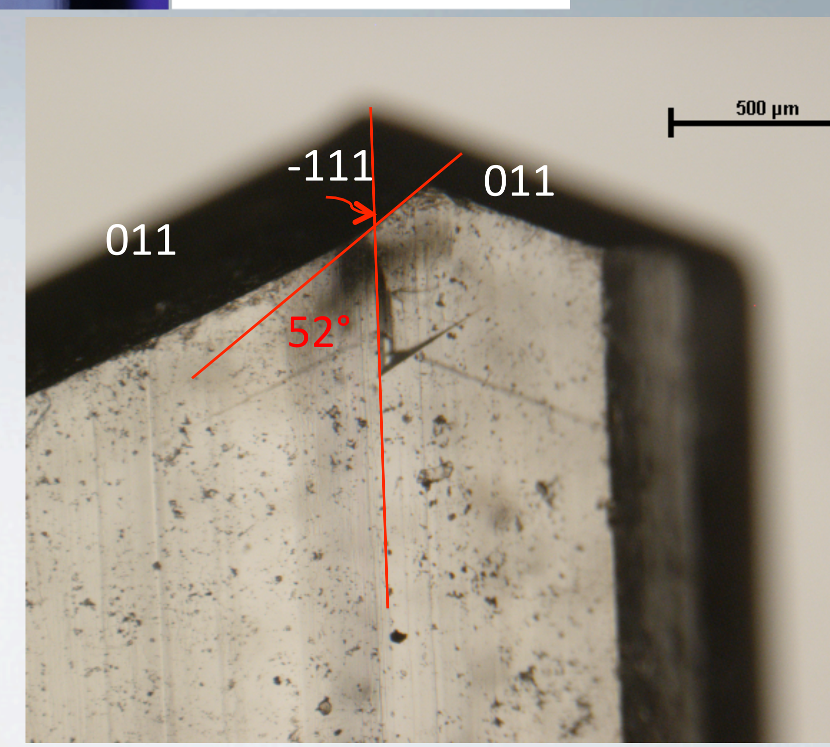

(010)
(1k0)

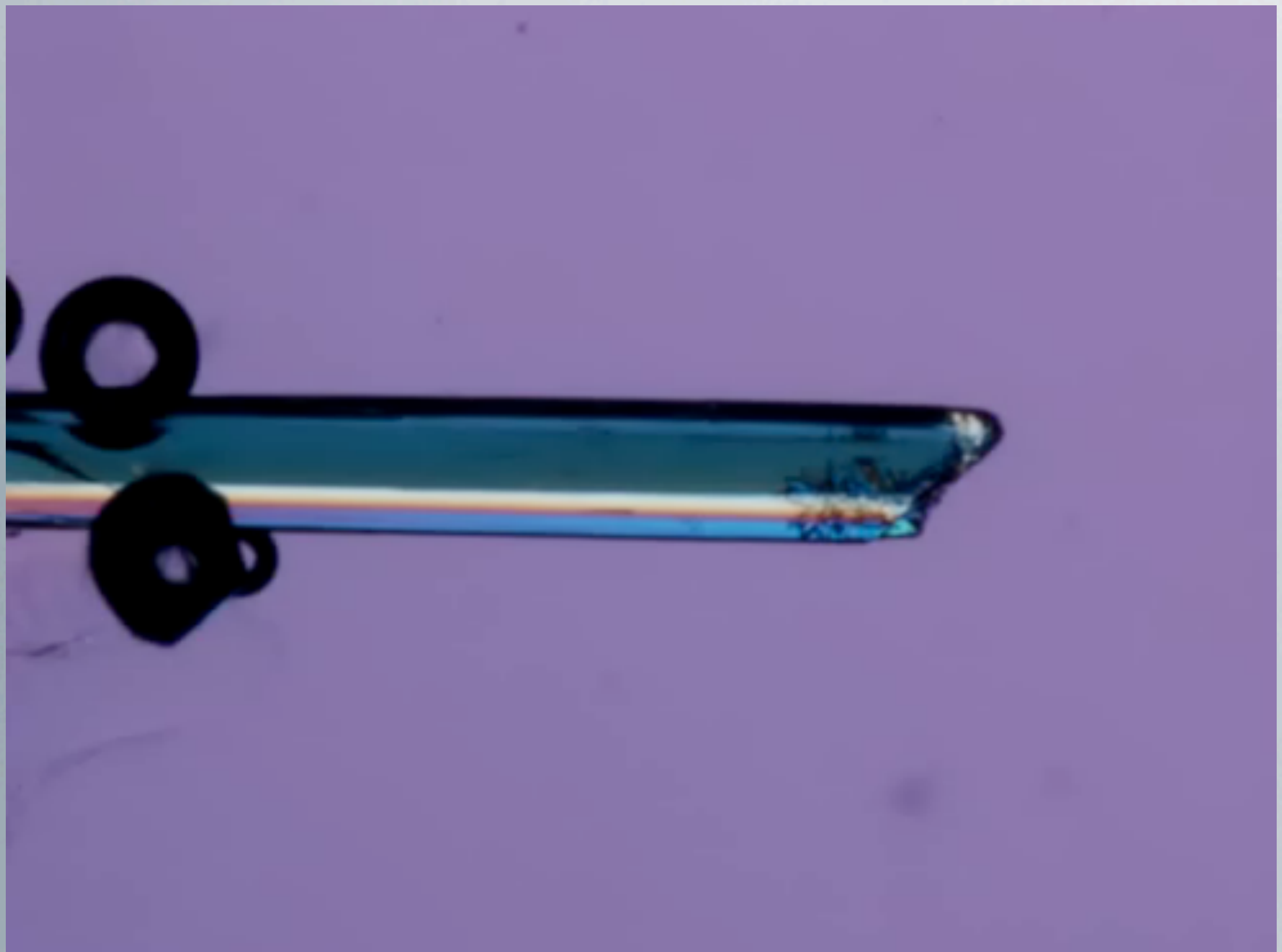


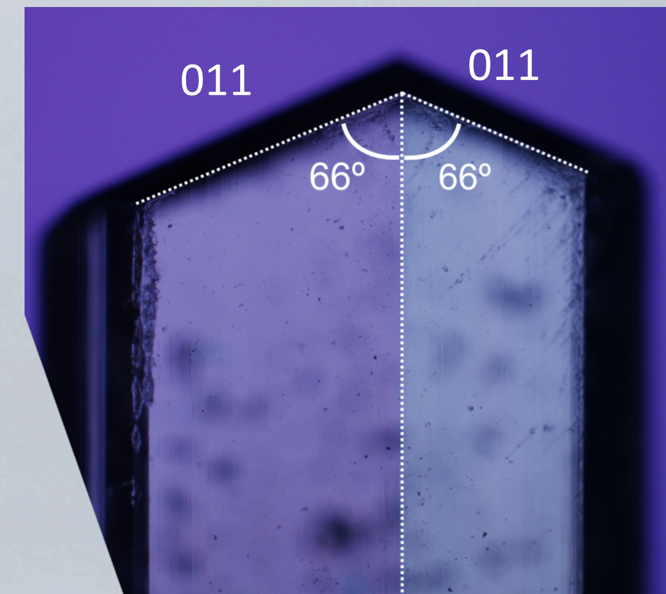


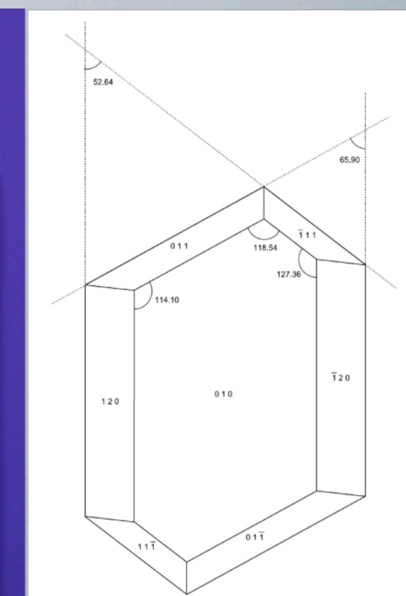
{010} Pinacoid
{1k0} Prism
{-111} Prism
{011} Prism









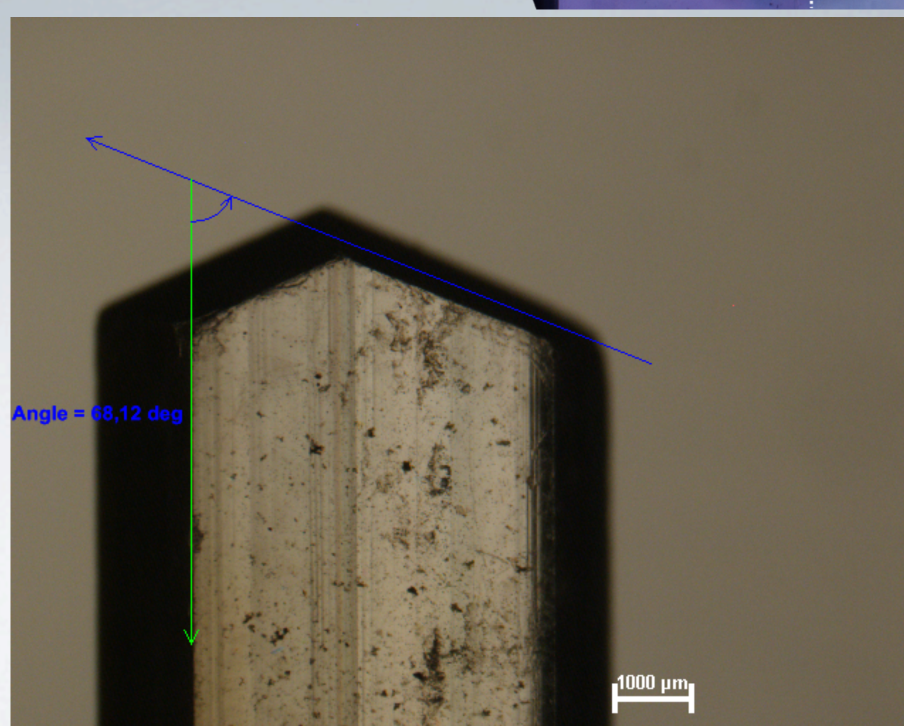


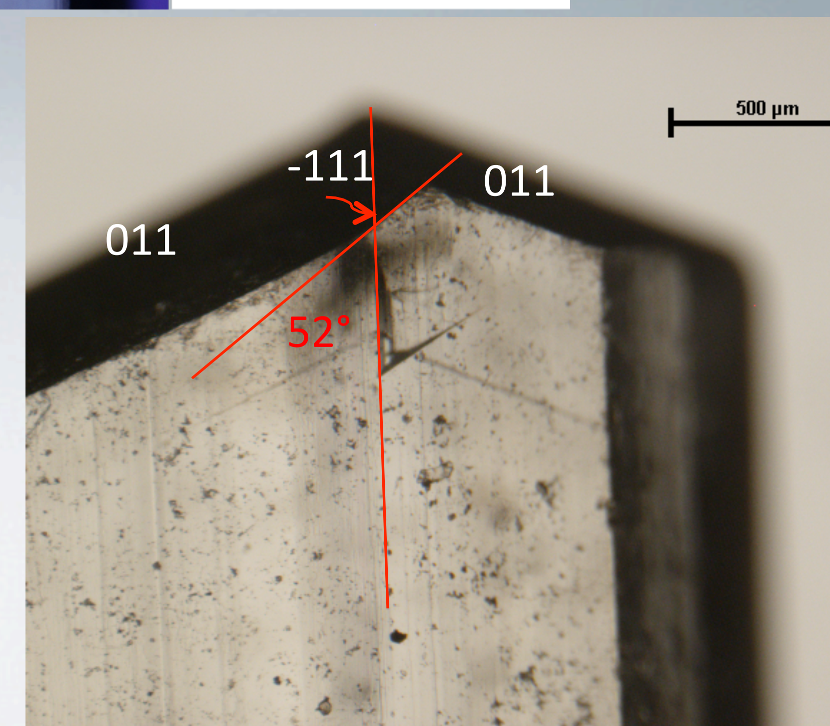
{010} Pinacoid

{1k0} Prism

{-111} Prism

{011} Prism





The symmetry of natural shapes

(classical thought)

The realm of the crystal

Inorganic symmetry

Polyhedral, faceted shapes
Deterministic angles
Forbidden symmetry operators

$32\ G^3_0 \subset K$

$A_i\gamma_i = \text{minimum}$



The realm of life

Organic symmetry

Sinuous shapes
Continuous curvature
Unrestricted symmetry

$\infty\ G^3_0 \not\subset K$

$A_i\gamma_i > \text{minimum}$




End of Pattern of the rocks I