

Crystal Growth: Physics, Technology and Modeling

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Lecture 11. Shape selection during growth and shape stability

<http://w3.unipress.waw.pl/~stach/cg-2022-23/>

Scope

- **Growth habit – flat and rough surfaces**
- **Flat surfaces – evolution of the faces**
- **Face stability**
- **Morphological stability of the rough surfaces**
- **Instability of the flat crystallization face**
- **Instability of spherical nucleus**
- **Shape evolution – emergence of dendrite**
- **Cellular instability**

Basic growth modes

- **Flat surface**
 - **Slow kinetics**
 - **High supersaturation**
 - **Growth shape – collection of crystallographic planes**

- **Rough surfaces**
 - **Fast kinetics**
 - **Small supersaturation**
 - **Surface shape – follows thermodynamics potential distribution**

Growth habit – set of crystallographic planes

- **Crystallographic plane identification - Miller (ijk) or Miller-Bravais (ijkl) indices - faces should be associated with the planes**
- **Face – fraction of crystallographic plane - face area $S_{(ijk)}$**
- **Face weights $w_{(ijk)}$**

$$w_{(ijk)} = \frac{S_{(ijk)}}{\sum_{(ijk)} S_{(ijk)}}$$

Growth shape

- **Shape – set of the surfaces (2-d objects) described by mathematical relations**
- **Flat surface crystals: Miller or Miller-Bravais indices and their weights**
- **Flat surface: equation describing its shape in 3-d space (single or some combination)**

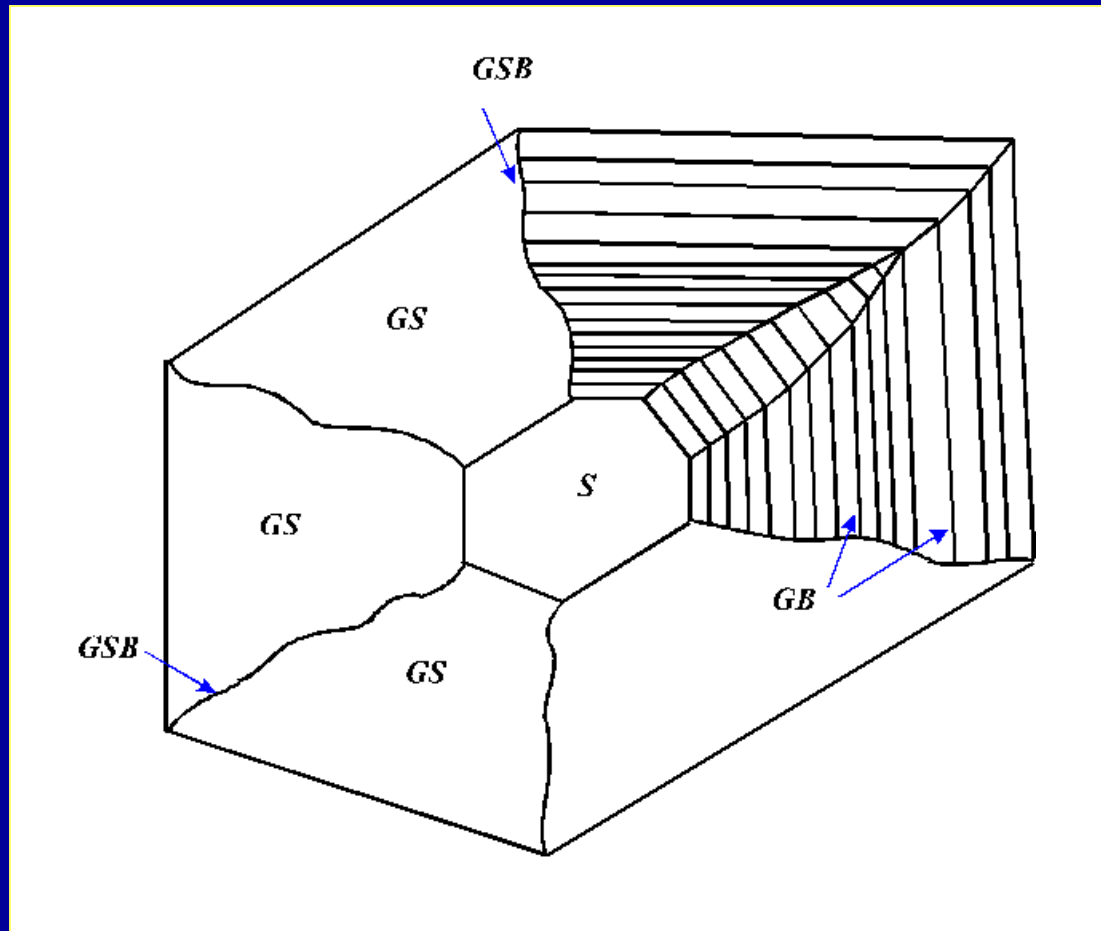
Flat surfaces – growth rates

- **Growth rate at crystallographic plane (face) – R_{hkl}**

$$R_{hkl} = \frac{[\vec{r}_{hkl}(t + \Delta t) - \vec{r}_{hkl}(t)] \cdot \vec{n}_{hkl}}{\Delta t}$$

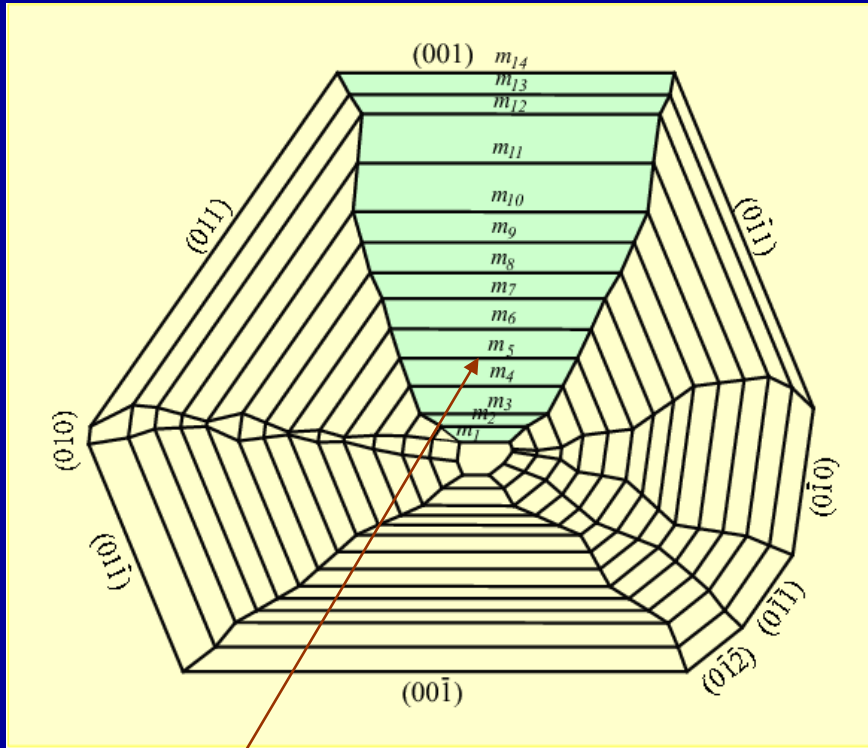
- **Shape change – geometric translation in the direction normal to the plane**
- **Shape evolution during growth – some faces may arise or disappear – face morphological stability**
- **Growth rates may depend on the local thermodynamic conditions**

Growth sectors, growth sector boundaries, growth bands

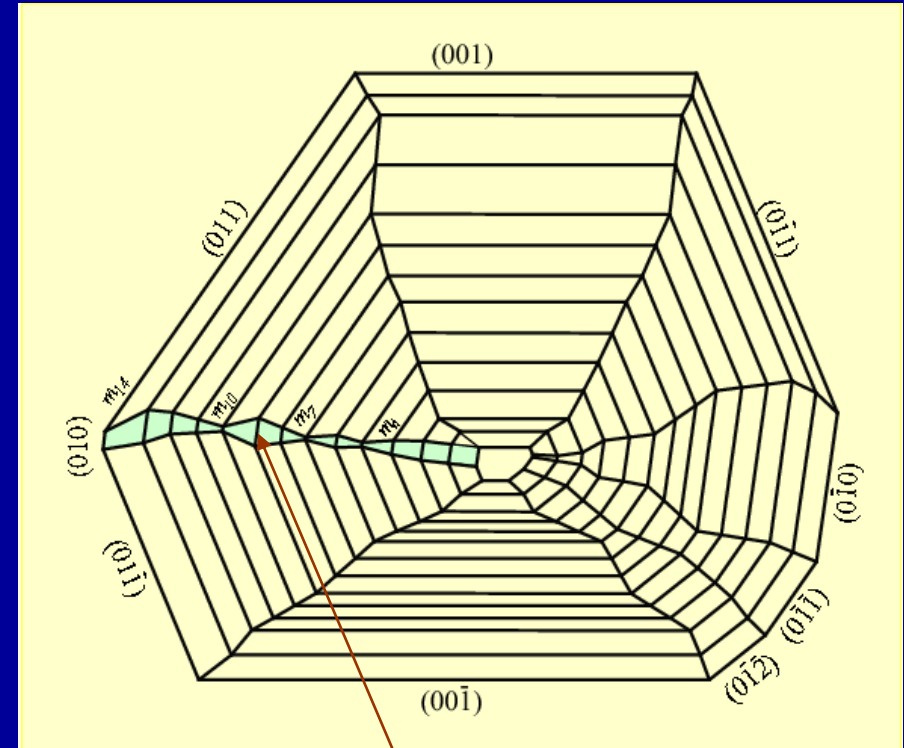


GS – growth sectors, GSB – growth sector boundaries , GB – growth bands, S - nucleus.

Face stability - (growth of potassium dichromate – $K_2Cr_2O_7$ - KBC)



Stable wall



Unstable wall

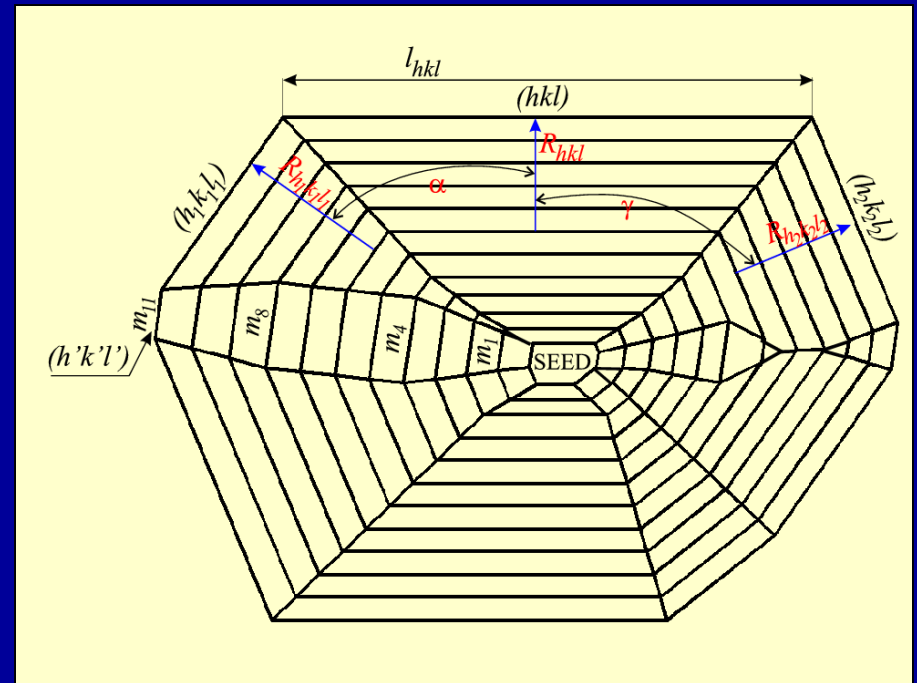
J. Prywer: "Crystal faces existence and morphological stability from crystallographic perspective" *Cryst. Growth Des.* **3** (2003) 593–598.

Tangential growth rate

$$\frac{dl_{hkl}}{dt} = \frac{R_{h_1k_1l_1}\sin(\gamma) + R_{h_2k_2l_2}\sin(\alpha) - R_{hkl}\sin(\alpha + \gamma)}{\sin(\alpha)\sin(\gamma)}$$

Tangential velocity dl_{hkl}/dt determines the face evolution:

- (i) $dl_{hkl}/dt > 0$ face (hkl) increases
- (ii) $dl_{hkl}/dt = 0$ face (hkl) is not changed
- (iii) $dl_{hkl}/dt < 0$ face (hkl) decreases



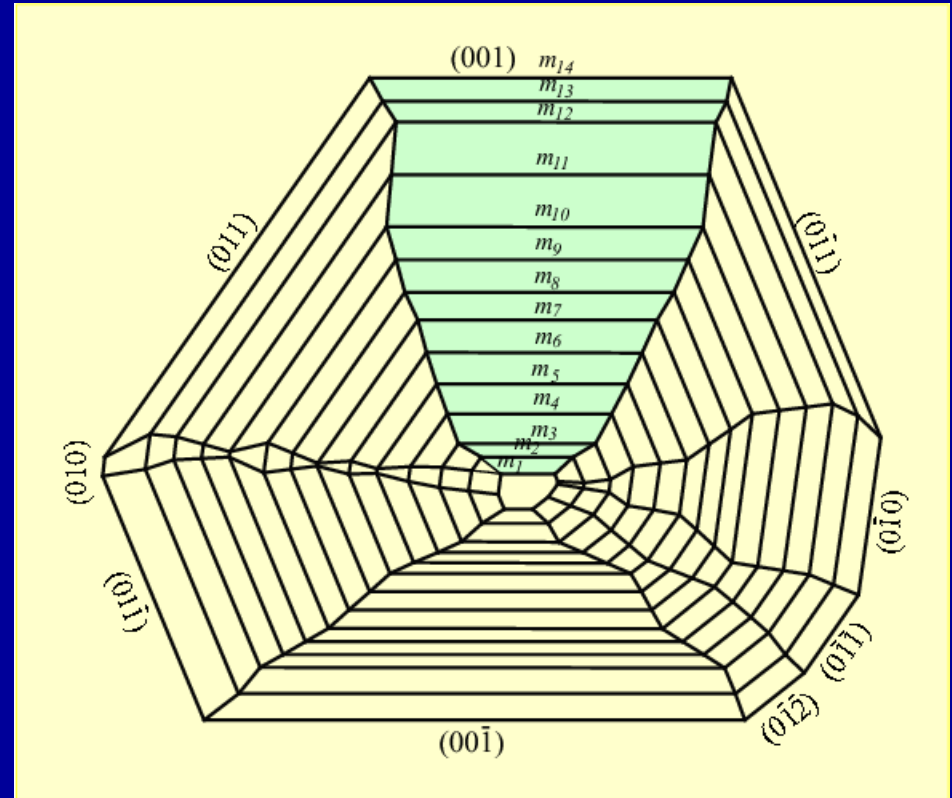
J. Prywer: "Crystal faces existence and morphological stability from crystallographic perspective" *Cryst. Growth Des.* **3** (2003) 593–598.

Morphological stability of the faces

face (001)

$\alpha = 54.90 \text{ arc deg}, \gamma = 72.79 \text{ arc deg}$

prążek	$\frac{R_{(001)}}{R_{(011)}}$	$\frac{R_{(001)}}{R_{(0\bar{1}1)}}$	$\frac{dl_{(001)}}{dt}$
	0-1	0.52	0.46
1-2	0.65	0.72	2.93
2-3	0.50	0.50	3.15
3-4; 4-5	1.14	1.14	2.05
5-6	1.20	1.20	1.92
6-7	1.25	1.25	1.81
7-8	1.05	1.05	2.26
8-9; 9-10	1.25	1.25	1.81
10-11	2.00	2.00	0.14
11-12	2.25	2.25	0.13
12-13	0.89	1.14	1.92
13-14	0.98	1.77	1.30



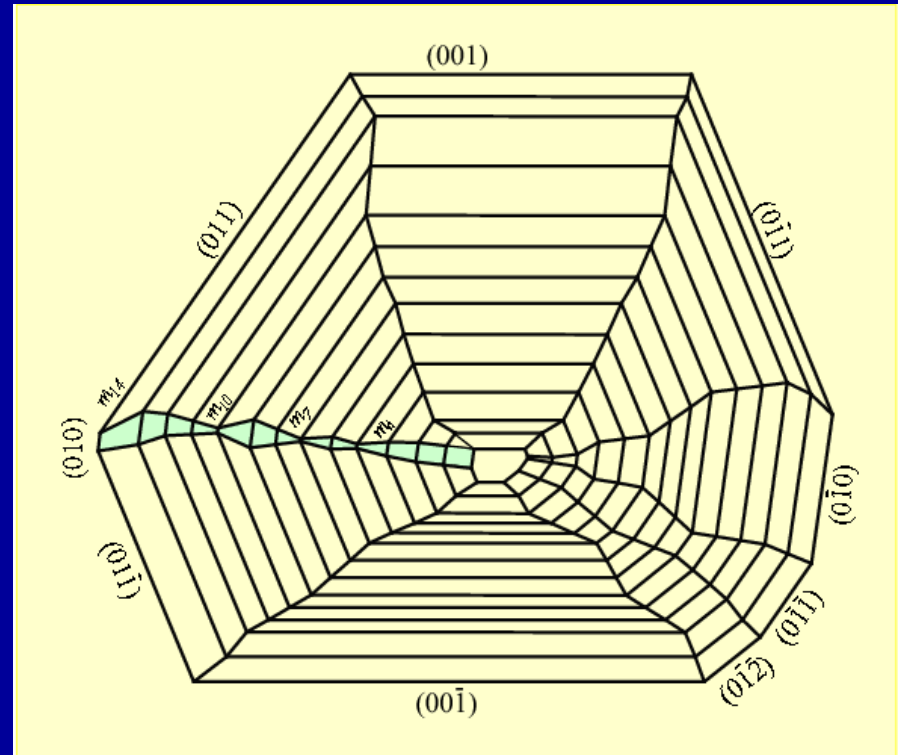
J. Prywer: "Crystal faces existence and morphological stability from crystallographic perspective" *Cryst. Growth Des.* **3** (2003) 593–598.

Morphological stability of the walls

Wall (010)

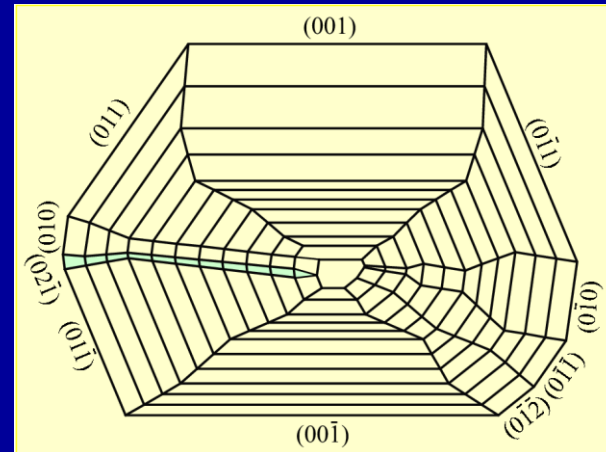
$\alpha = 30.80 \text{ arc deg}, \gamma = 27.01 \text{ arc deg}$

prążek	$R_{(010)}$	$R_{(010)}$	$dl_{(010)}$
	$R_{(01\bar{1})}$	$R_{(011)}$	dt
0-1	1.00	0.72	2.47
1-2; 2-3	1.14	1.14	0.00
3-4	1.20	1.20	-0.42
4-5	1.25	1.25	-0.79
5-6	1.05	1.05	0.67
6-7	1.25	1.25	-0.79
7-8; 8-9	1.00	1.00	1.03
9-10	1.40	1.40	-1.88
10-11; 11-12	1.05	1.05	0.67
12-13	0.89	1.14	0.99
13-14	0.98	1.77	-1.28



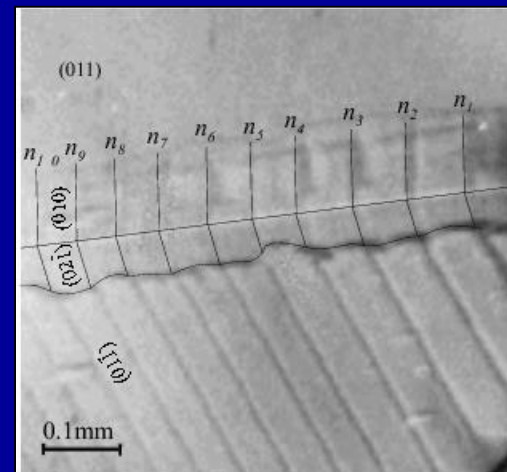
J. Prywer: "Crystal faces existence and morphological stability from crystallographic perspective" *Cryst. Growth Des.* **3** (2003) 593–598.

Morphological stability of the faces



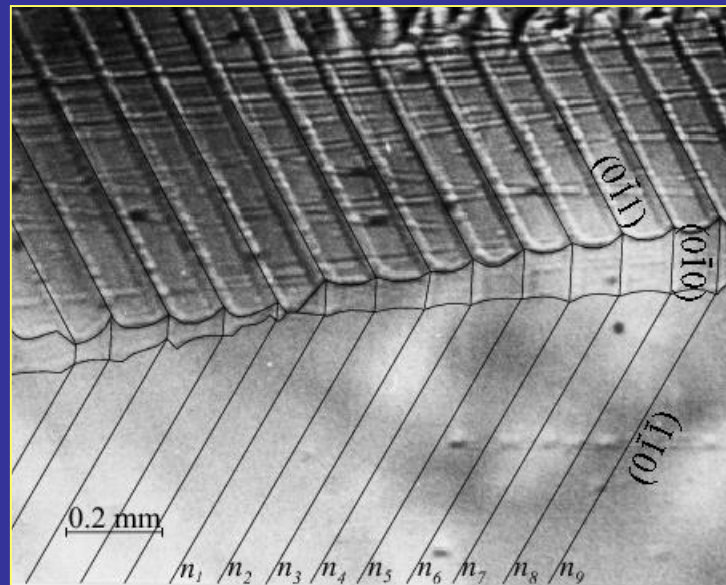
Face $(02\bar{1})$

$\alpha = 14.84 \text{ arc deg}$, $\gamma = 15.96 \text{ arc deg}$



J. Prywer: "Crystal faces existence and morphological stability from crystallographic perspective" *Cryst. Growth Des.* **3** (2003) 593–598.

Morphological stability of the faces – KBC (0 $\bar{1}0$) surface



J. Prywer: "On the crystal geometry influence on the growth of fast-growing surfaces",
J. Phys. and Chem. of Solids **63** (2002) 493–501.

Bravais-Friedel-Donnay-Harker (BFDH) law

Morphological weight (MI) of the faces is proportional to interplanar distance

$$d_{h_1k_1l_1} > d_{h_2k_2l_2} \Rightarrow \text{MI}_{h_1k_1l_1} > \text{MI}_{h_2k_2l_2}$$

$$R_{hkl} \propto 1/d_{hkl}$$

MI (morphological importance)

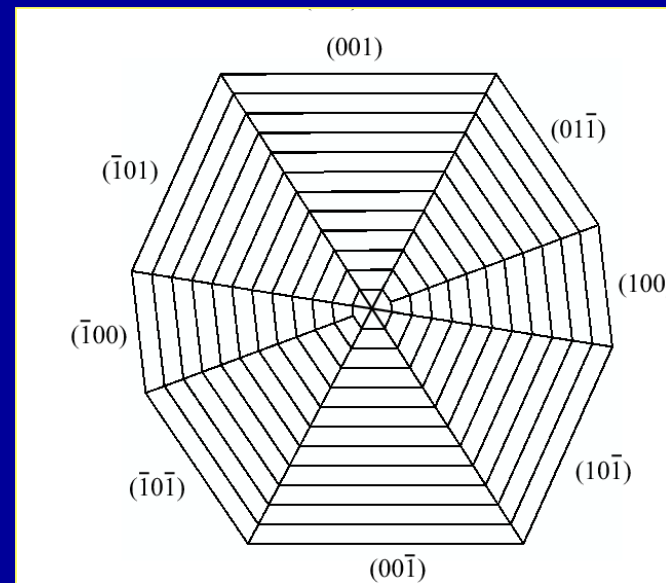
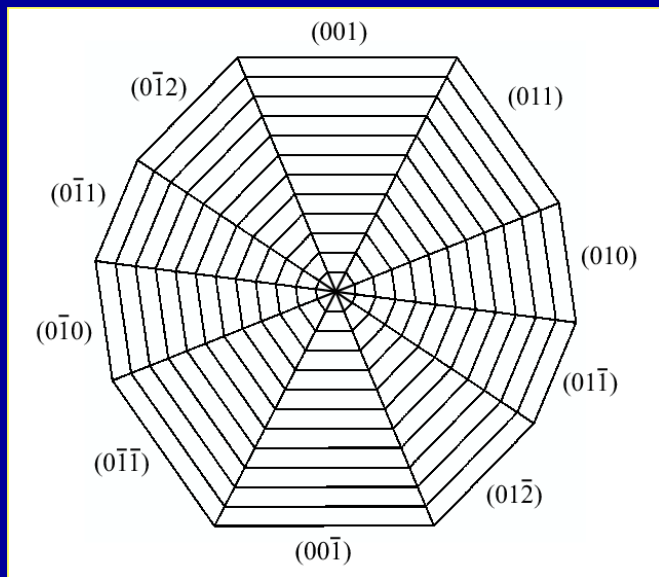
G. Friedel, *Leçon de Cristallographie*, Hermann, Paris (1911).

A. Bravais, *Études Cristallographiques*, Gauthier-Villard, Paris (1913).

J.D.H. Donnay, D. Harker, *Am. Mineral.* 22 (1937) 446.

Face morphological importance (MI)

All faces have the same growth rate – morphological importance is different



J. Prywer: "Kinetic and Geometric Determination of the Growth Morphology of Bulk Crystals: Recent Developments" *Prog. Cryst. Growth Charact.* **50** (2005) 1–38.

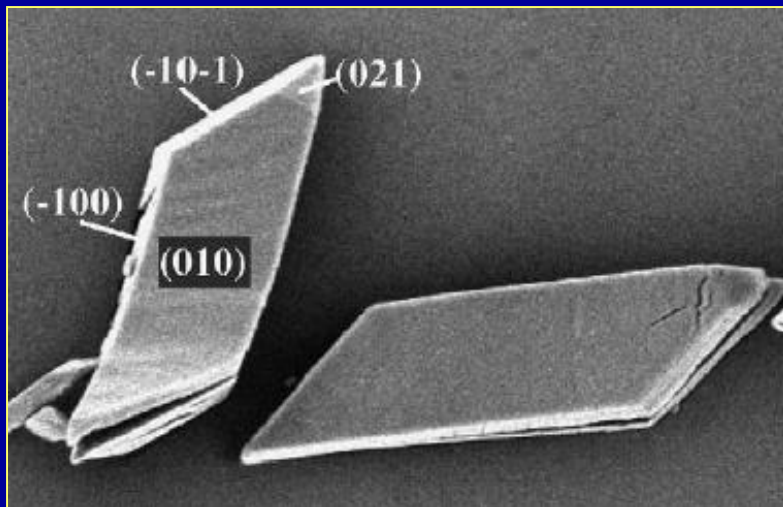
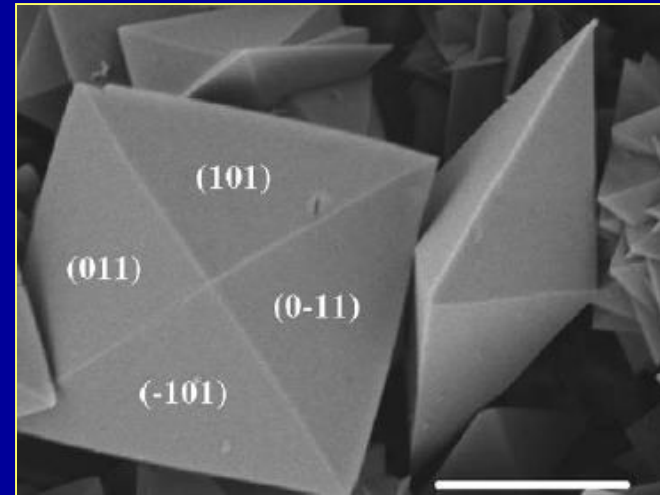
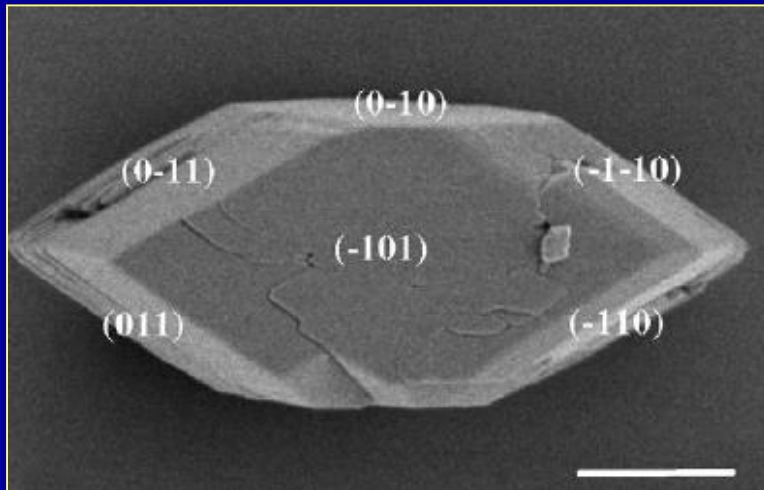
Growth rate rules

- Attachment energy rule (Hartmann et al.)

$$R_{hkl} \propto E_{hkl}$$

E_{hkl} – attachment energy – energy change during attachment of new atomic layer at given crystallographic plane

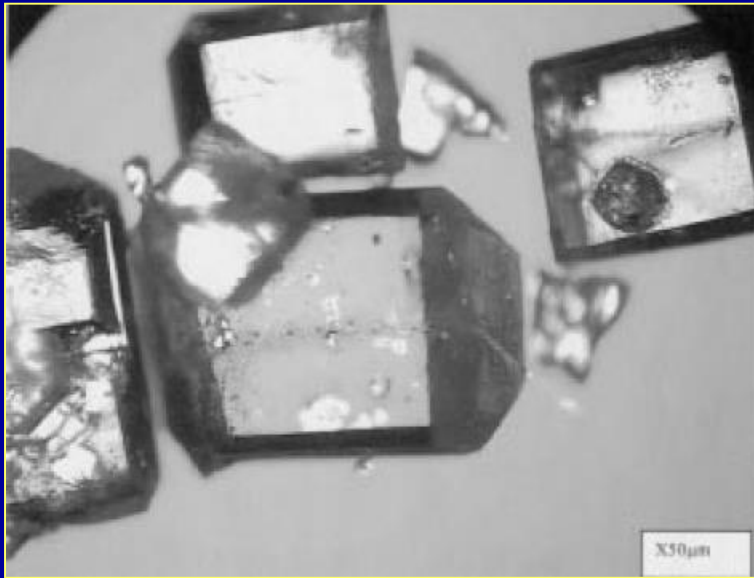
Calcium oxalate - $\text{CaC}_2\text{O}_4 \cdot (\text{H}_2\text{O})_x$



R. C. Walton, J.P. Kavanagh, B. R. Heywoodb,
P. N. Rao,
*Calcium oxalates grown in human urine under
different batch conditions.*
J. Cryst. Growth 284 (2005) 517

Pharmaceutics

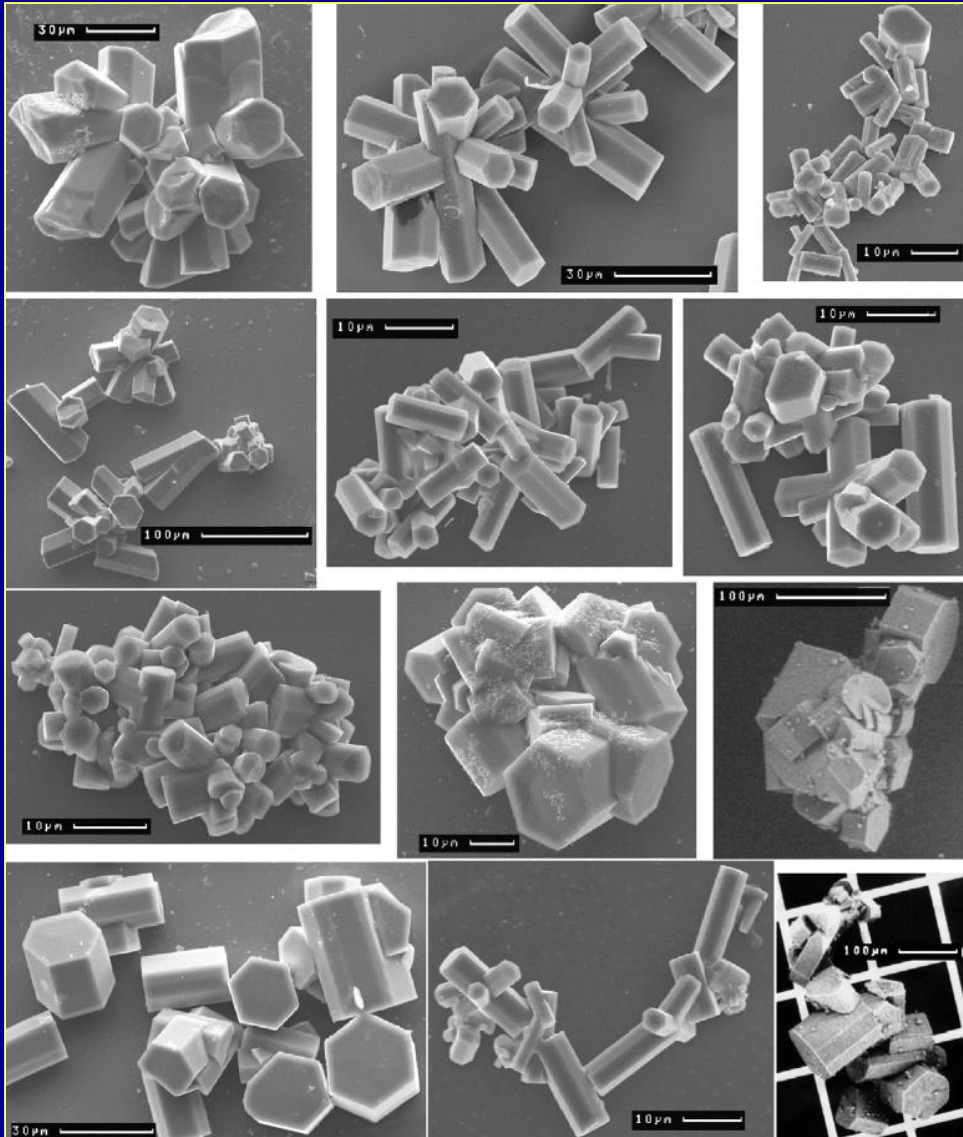
Ascorbic Acid – C₆H₈O



Vitamin C crystals grown from water solution by slow evaporation.

**A. Arslants, W.C. Emler, R. Yazici, D. M. Kalyon,
Crystal Habit Modification of Vitamin C (L-Ascorbic Acid) due to Solvent Effects.
Turk. J. Chem. 28 (2004) 255**

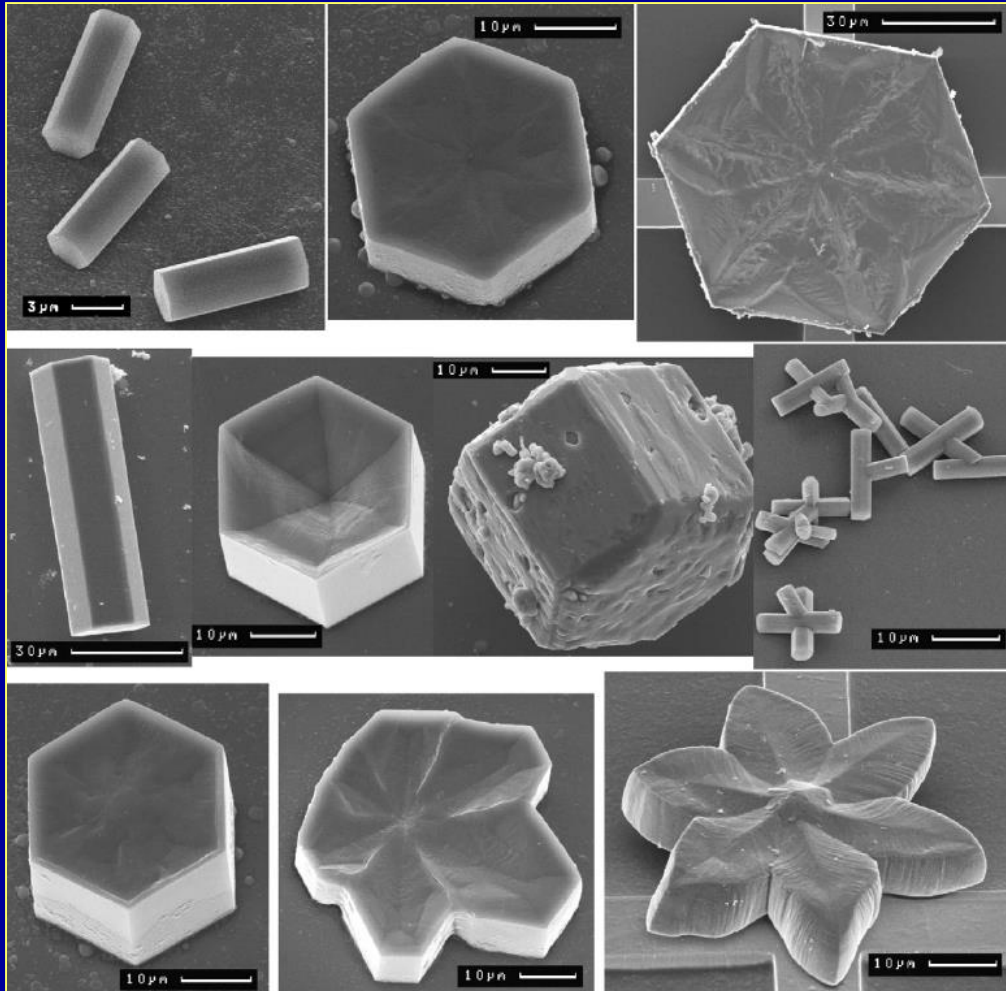
Na_2SiF_6 – crystal analogy to ice



Z. Ulanowski, E. Hessea, P. H. Kayea, A. J. Baranb, R Chandrasekhar,
Scattering of light from atmospheric ice analogues.

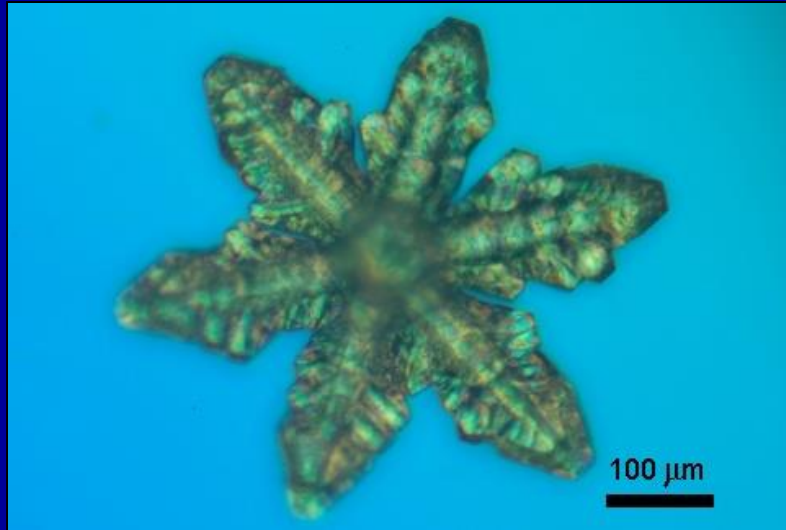
J. Quant. Spectr. Radiat. Transfer 79-80
(2003) 1091

Na_2SiF_6 – crystal analogy to ice



Z. Ulanowski, E. Hessea, P. H. Kayea,
A. J. Baranb, R Chandrasekhar,
*Scattering of light from atmospheric
ice analogues* .
J. Qant. Spetcr. Radiat. Transfer 79-
80 (2003) 1091

Na_2SiF_6 – crystal analogy to ice



Crystal grown in Institute of Physics
Lodz University of Technology



Crystal grown in Hertforshire University
<http://strc.herts.ac.uk/ls/analog.html>

M. J. Krasinski, J. Prywer: "Growth morphology of sodium fluorosilicate crystals and its analysis in base of relative growth rates" – *J. Cryst. Growth* **303** (2007) 105–109.

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Morphological stability – preservation of the shape during growth

- **Morphology change – emergence of the new shape (local difference) is defined as the shape (morphology) instability**

Instability modes:

- **Surface (plane)**
- **Edge - corner**
- **Sphere**

Linear stability theory

- **Basic solution (stationary)**

$$f = f_o(\vec{r}, t) = f(\vec{r} - \vec{v}t)_o$$

- **Perturbed solution**

$$f = f_o(\vec{r}, t) + \delta(\vec{r}, t) \quad |\delta(\vec{r}, t)| \ll |f_o(\vec{r}, t)|$$

- **Linearization of the equation – matrix linear equation**

$$\frac{d\delta(\vec{r}, t)}{dt} = A \delta(\vec{r}, t)$$

- **Solution of the linear equation**

$$\delta(\vec{r}, t) = \delta(\vec{r}) \exp(\lambda t)$$

λ – Lyapunov exponent

$$\lambda > 0 \quad \textit{unstable}$$

$$\lambda < 0 \quad \textit{stable}$$

Flat crystallization front – growth from solution

- Temperature and concentration equations (**solid, liquid**)

$$\frac{\partial T}{\partial t} = D_{th}\Delta T$$

$$C_s = \text{const}(t)$$

$$\frac{\partial T}{\partial t} = D_{th}\Delta T$$

$$\frac{\partial C_l}{\partial t} = D_l\Delta C_l$$

- Boundary conditions $z = vt$

$$T_s = T_l = T_M \left(1 + \frac{2\Gamma}{R} + m_l C_l \right)$$

$$C_s = kC_l$$

$$\kappa_s \nabla T_s = \kappa_k \nabla T_l + \vec{v}H$$

$$D_l \nabla C_l = \vec{v}(k - 1)C_l$$

- Solution – stationary in the interface coordination system

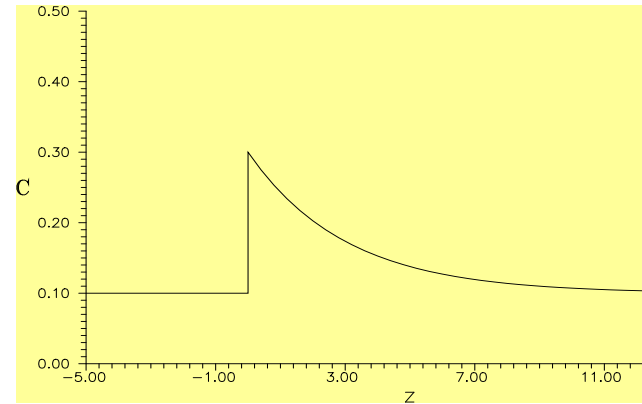
Flat crystallization front

- Concentration**

$$C_l = C_s + C_s \frac{1-k}{k} \exp\left[-\frac{vz}{D}\right]$$

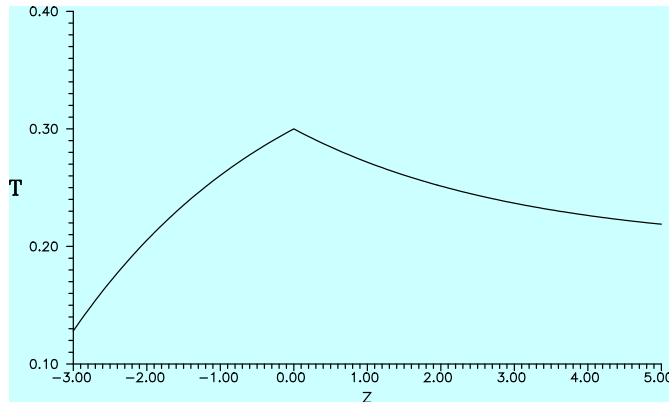
$$= C_s + \frac{GD}{v} \exp\left[-\frac{vz}{D}\right]$$

G – solute gradient at interface

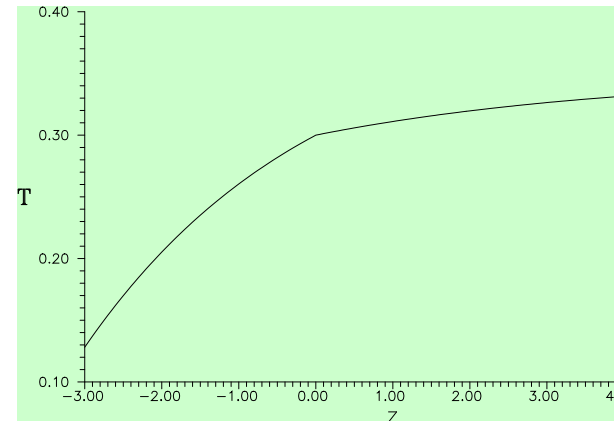


- Temperature**

$$T_{l,s} = T_M - \frac{G_{l,s}D_{l,s}}{v} \left\{ 1 - \exp\left[-\frac{vz}{D_{th,l,s}}\right] \right\}$$



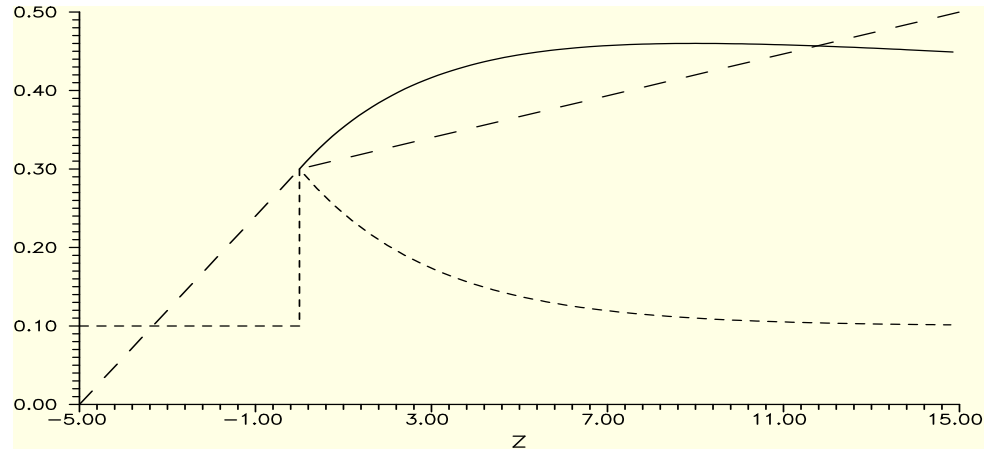
Liquid supercooling $G_L < 0$



No liquid supercooling $G_L > 0$

Constitutional supercooling at flat front

- **Effective melting temperature: $T_1 = T_M + m C_l$**



$$T \cong G_S \Theta(1 - z) + G_l \Theta(z) \qquad C = C_S + \frac{GD}{v} \exp\left[-\frac{vz}{D}\right]$$

- **Constitutive supercooling condition: $G_l < m G$**

J. W. Rutter and B. Chalmers, *Can. J. Phys.* 31 (1953) 15

W. A. Tiller, J. W. Rutter, K. A. Jackson and B. Chalmers, *Acta Met.* 1 (1953) 729

Mullins –Sekerka theory of morphological stability

- Linear stability theory**

$$C(\vec{r}, t) = C(z) + \delta C \exp(\pm qz + \lambda t) \cos(\omega x)$$

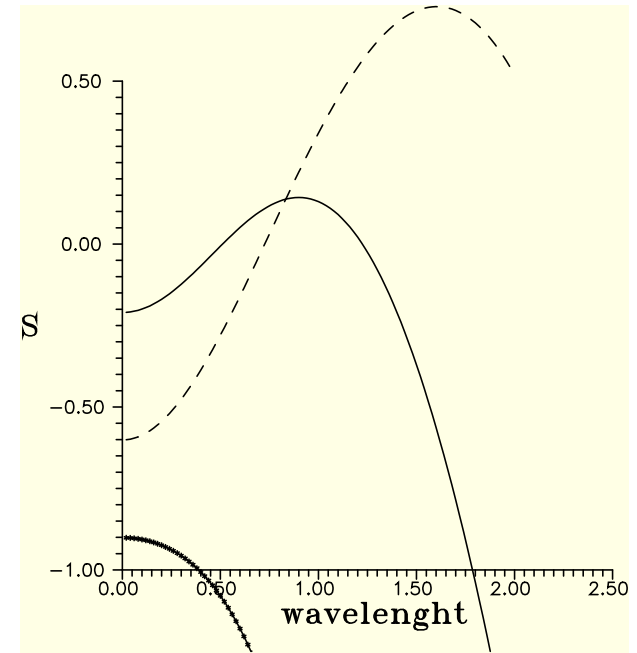
$$T(\vec{r}, t) = T(z) + \delta T \exp(\pm qz + \lambda t) \cos(\omega x)$$

$$z(\vec{r}, t) = \delta z \exp(\lambda t) \cos(\omega x)$$

- Stability condition – Lyapunov exponent**

$$S = \frac{v\omega \left\{ (-2T_M \Gamma \omega^2 - G_l + G_s) \left[q + \frac{(1-k)v}{D} \right] - 2mG \left[q - \frac{v}{D} \right] \right\}}{(G_l - G_s) \left[q - \frac{(1-k)v}{D} \right] + 2kmG}$$

$$q = \frac{v}{2D} \pm \sqrt{\left(\frac{v}{2D}\right)^2 + \omega^2}$$

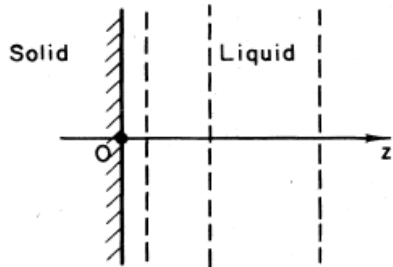


W.W. Mullins & R.F. Sekerka, J. Appl. Phys. 35 (1964) 444

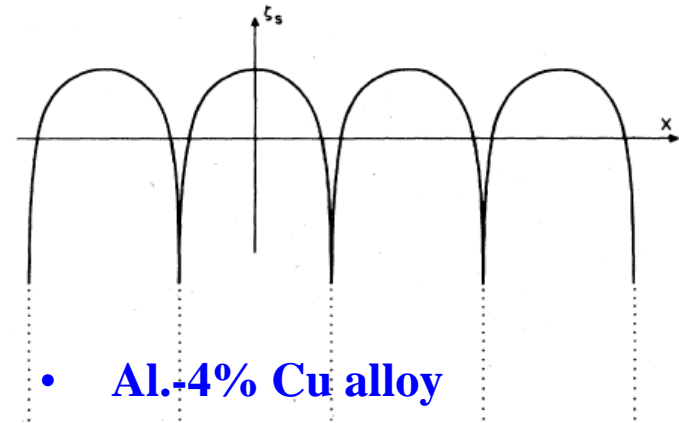
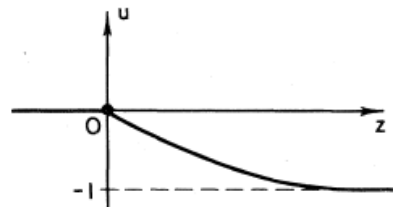
Mullins –Sekerka instability of flat surface – cellular growth

- Instability mechanism

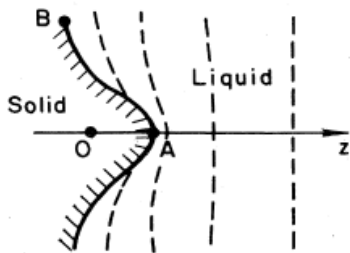
- Cellular interface



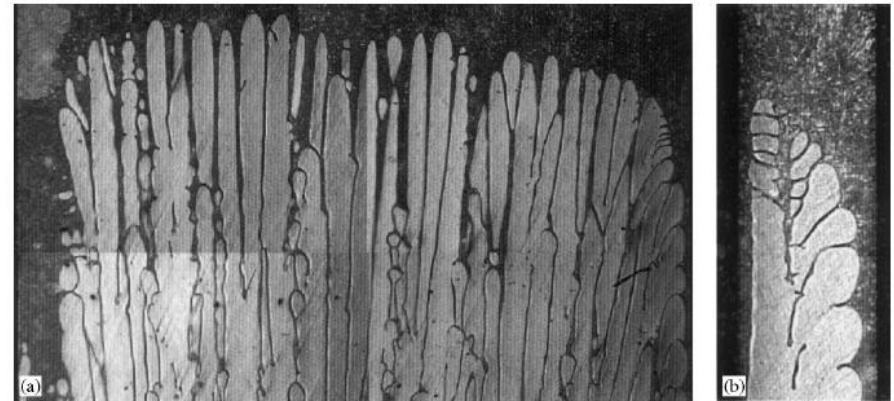
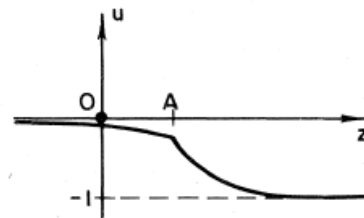
(a)



• Al-4% Cu alloy



(b)



J.S. Langer, Rev. Mod. Phys. 52 (1980) 1

R. Trvedi et al. J. Cryst. Growth 222 (2001) 365

Instability of growing spherical nucleus – Mullins-Sekerka theory

- **Diffusion**

$$\frac{\partial C}{\partial t} = D\Delta C = 0$$

- **Boundary condition**

$$C = C_o \left(1 - \frac{2\Gamma}{R} \right)$$

- **Stationary solution**

$$C(r) = C_1 + \frac{C_2}{r}$$

- **Linear stability analysis**

$$C(\vec{r}, t) = C(r) + \delta C(\vec{r}, t) = C(r) + \delta C_1(\vec{r}) \exp(\lambda t)$$

$$R(\vec{r}, t) = R + \delta(t) Y_l^m(\theta, \varphi) = R + \delta_o Y_l^m(\theta, \varphi) \exp(\lambda t)$$

Mullins & Sekerka result (Lyapunov exponent)

$$\lambda = \frac{D(l-1)}{GR^2} \left[G - \frac{\Gamma c_o(l+1)(l+2)}{R^2} \right]$$

$$R > 7R_{cr} \quad \lambda > 0 \quad \text{- unstable}$$

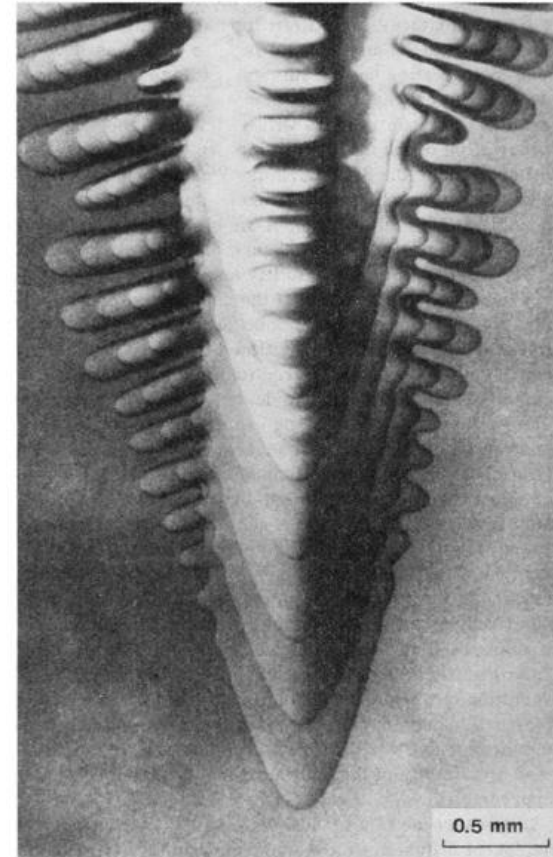
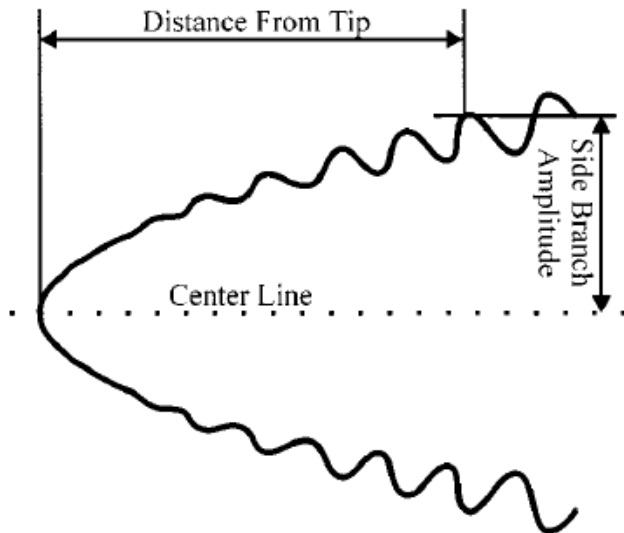
$$R < 7R_{cr} \quad \lambda < 0 \quad \text{- stable}$$

$$R_{cr} = \frac{2\Gamma}{\sigma} = \frac{2\gamma}{\Delta H} \frac{c_{eq}}{c_{\infty} - c_{eq}}$$

Side instability – evolution of dendrite - sidebranching

Dendrite – growth of first and secondary sidebranches

Dendrite – side has larger radius



S.D.P. Corrigan et al. Phys. Rev E 60 (1999) 7217

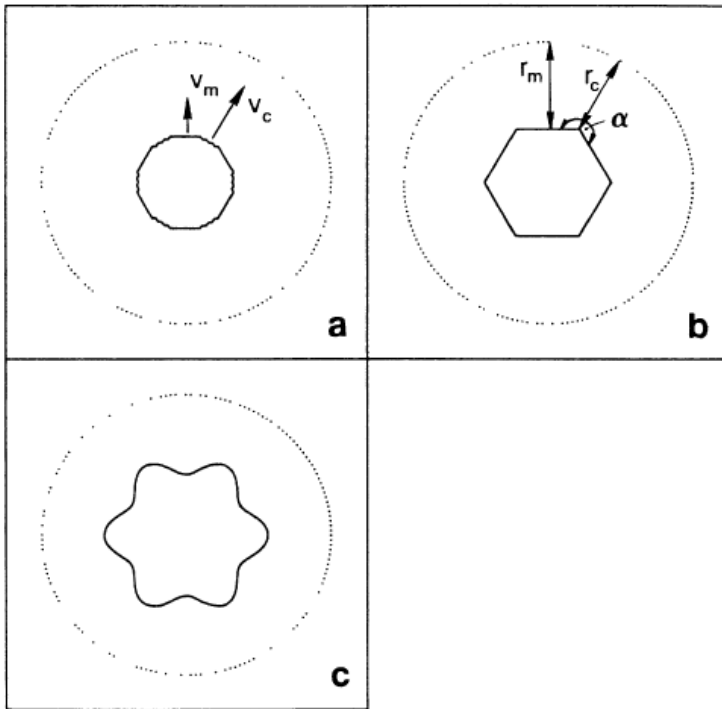
S.C. Huang & M.E. Glicksman,
Acta Metall. 29 (1981) 701

Edge instability in diffusion field

- Polyhedral shape \rightarrow Edge instability \rightarrow Needle effect \rightarrow Higher rate

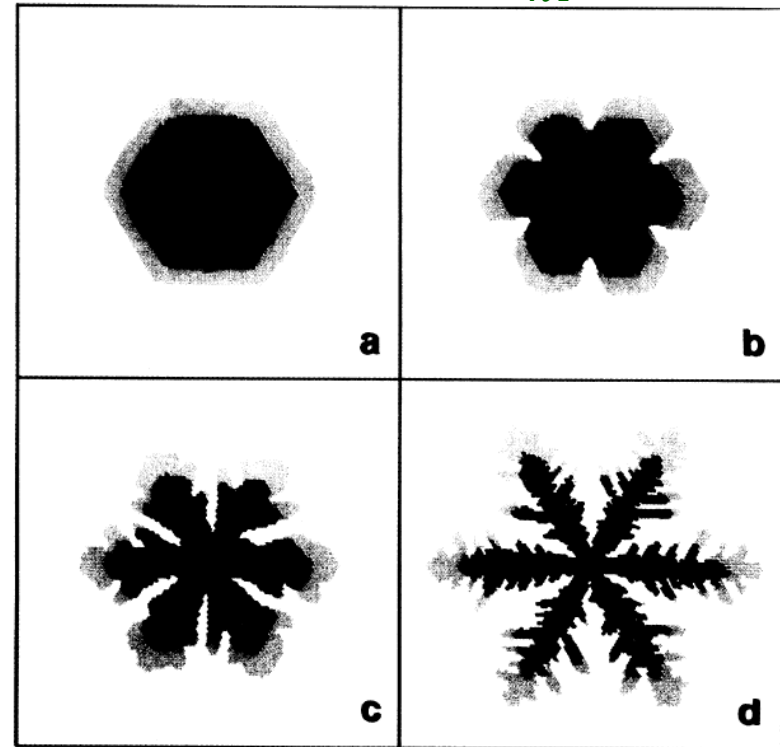
$$\sigma = 0.69$$

Angular access



$$\frac{\phi}{kT} = 3.91$$

$$\frac{\phi}{kT} = 2.3$$



R.F Xiao, J.I .D. Alexander & F. Rosenberger,
Phys. Rev A 38 (1988) 2447

$$\frac{\phi}{kT} = 0.69$$

$$\frac{\phi}{kT} = 0.36$$

Edge instability in ballistic/diffusive transport field

- Polyhedral shape \rightarrow Edge instability \rightarrow needle effect \rightarrow higher rate

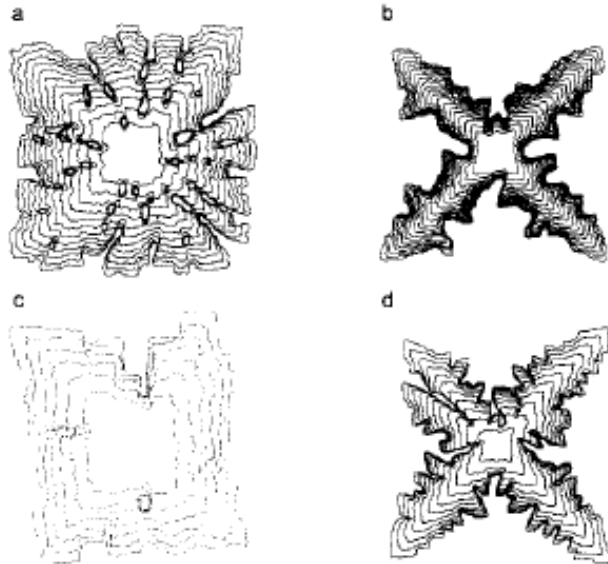
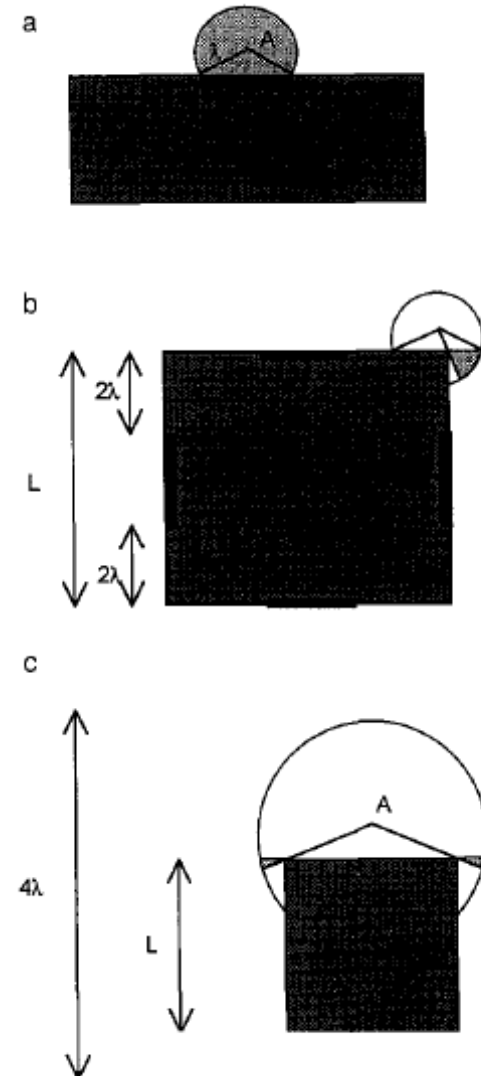
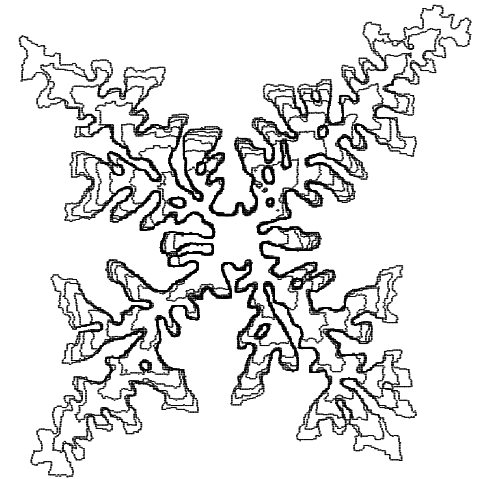
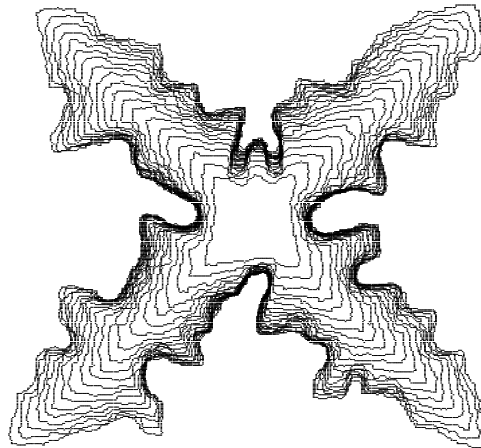
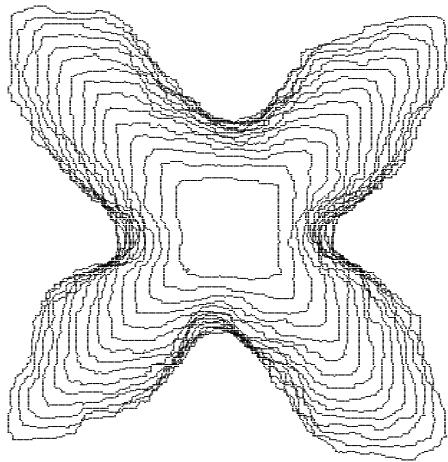


Fig. 7. Ballistic and diffusive transport modes: (a) $\lambda = 100a$; (b) $\lambda = 10a$, $L \approx 400a$; (c) $\lambda = 50a$, $L \approx 100a$; (d) $\lambda = 50a$, $L \approx 400a$. The other parameters are: $\epsilon = 6.0$, $\sigma = 1999$ and $\xi = 0.0$.



Edge instability – evolution to dendrite

- Polyhedral shape → Edge instability → needle effect → higher rate



- Side instability → sidebranching → dendrites

S. Krukowski & J.C. Tedenac, J. Cryst. Growth 203 (1999) 269

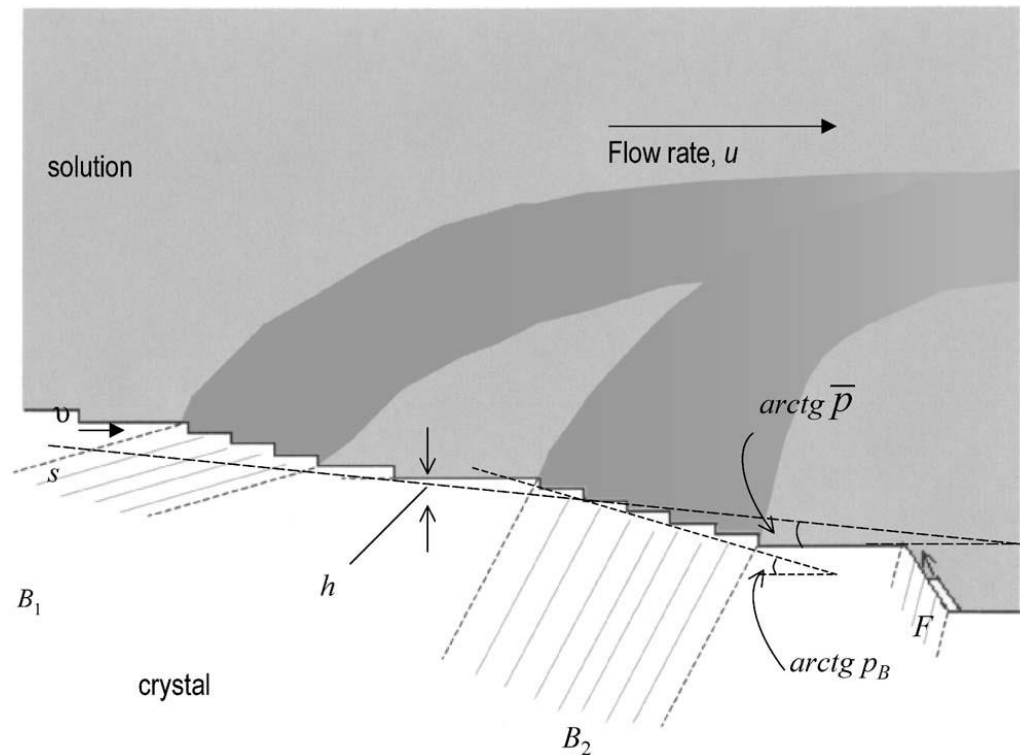
Snow crystals - dendrites



<http://www.its.caltech.edu/~atomic/snowcrystals/photos/photos.htm>

Microscopic scenario of instability

- **Morphological instability - step motion perturbation – coupling of transport and surface dynamics**



A. Chernov, J. Cryst. Growth 264 (2004) 599

Acknowledgments

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from Institute of Physics of Lodz University of Technology**

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