Crystal Growth: Physics, Technology and Modeling

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Lecture 11. Shape selection during growth and shape stability

http://www.unipress.waw.pl/~stach/cg-2021-22

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}**

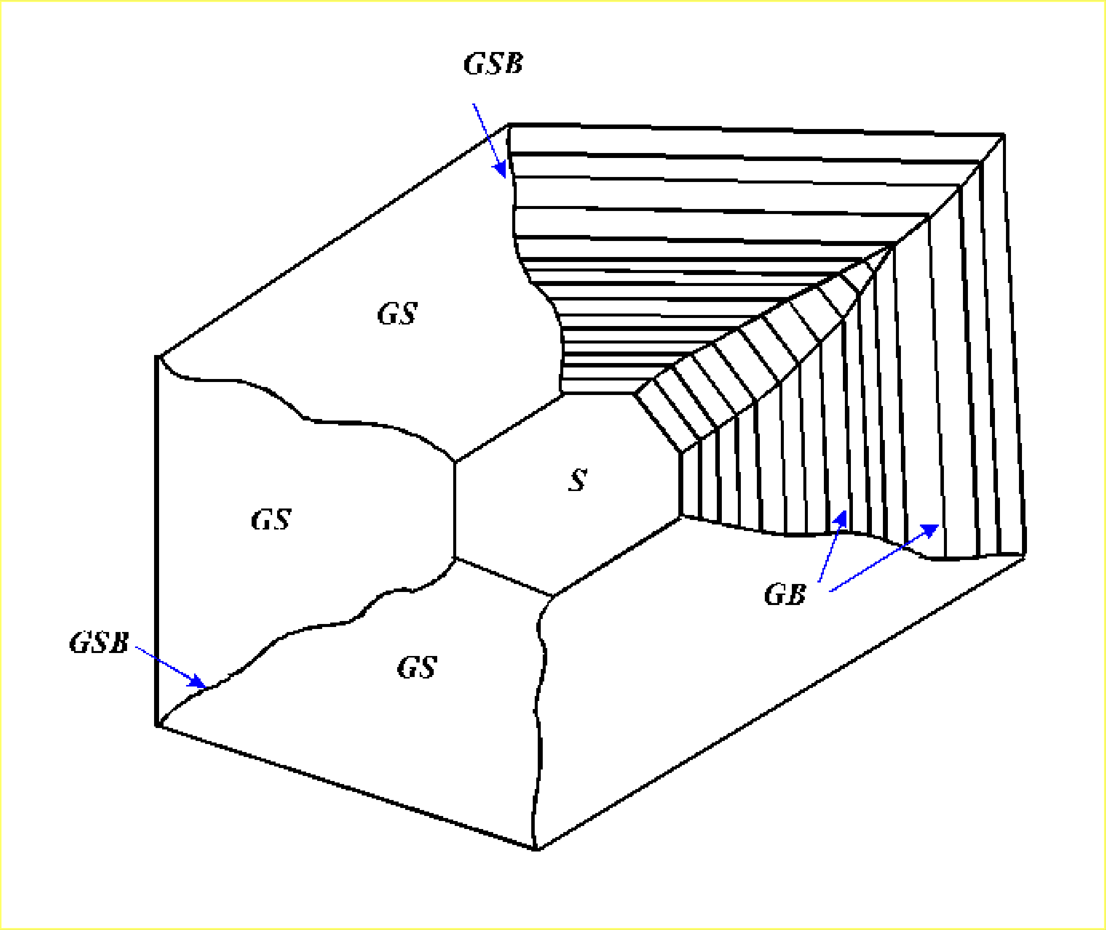
$$R_{hkl} = \frac{[\vec{r}_{hkl}(t + \Delta t) - \vec{r}_{hkl}(t)] \cdot \vec{n}_{hkl}}{\Delta t}$$

- **Shape change – geometric translation in the direction normal to the plane**

- **Shape evolution during growth – some faces may arise or disappear – face morphological stability**

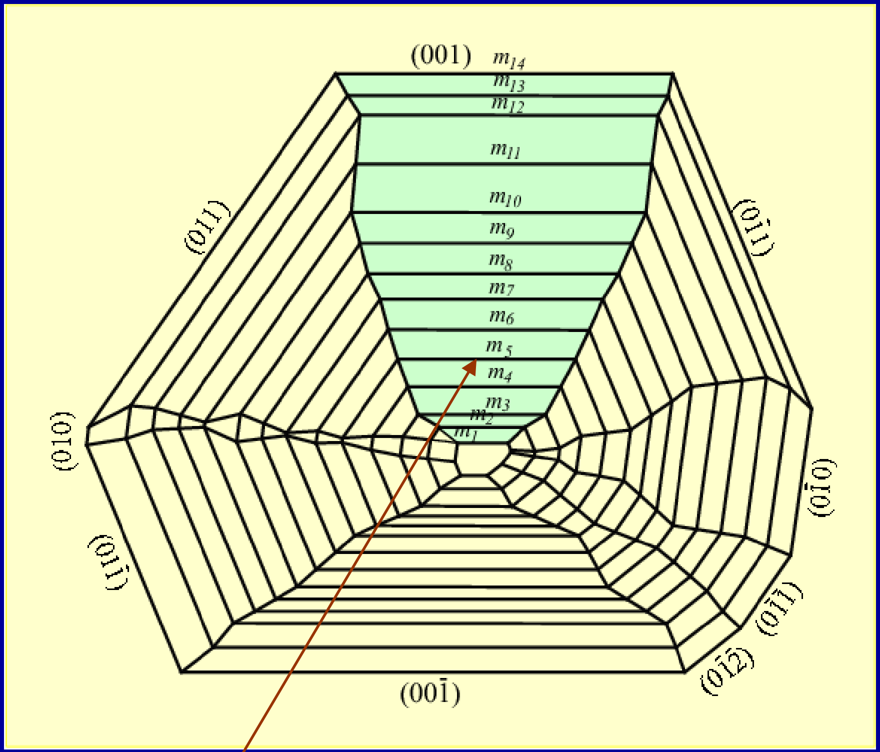
- **Growth rates may depend on the local thermodynamic conditions**

Growth sectors, growth sector boundaries, growth bands

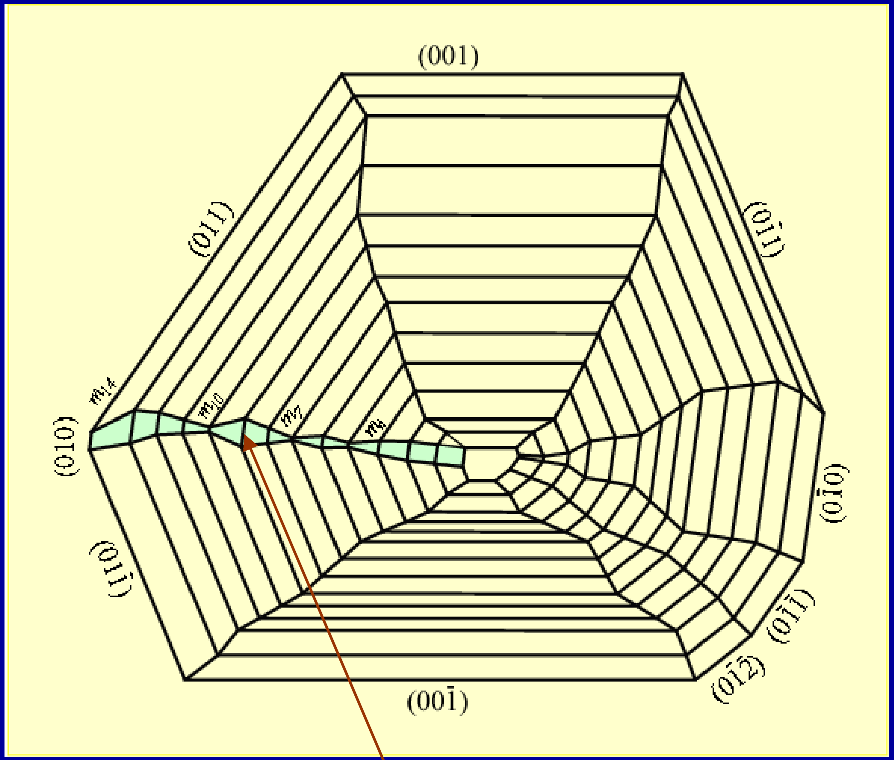


GS – growth sectors, GSB – growth sector boundaries , GB – growth bands, S - nucleus.

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

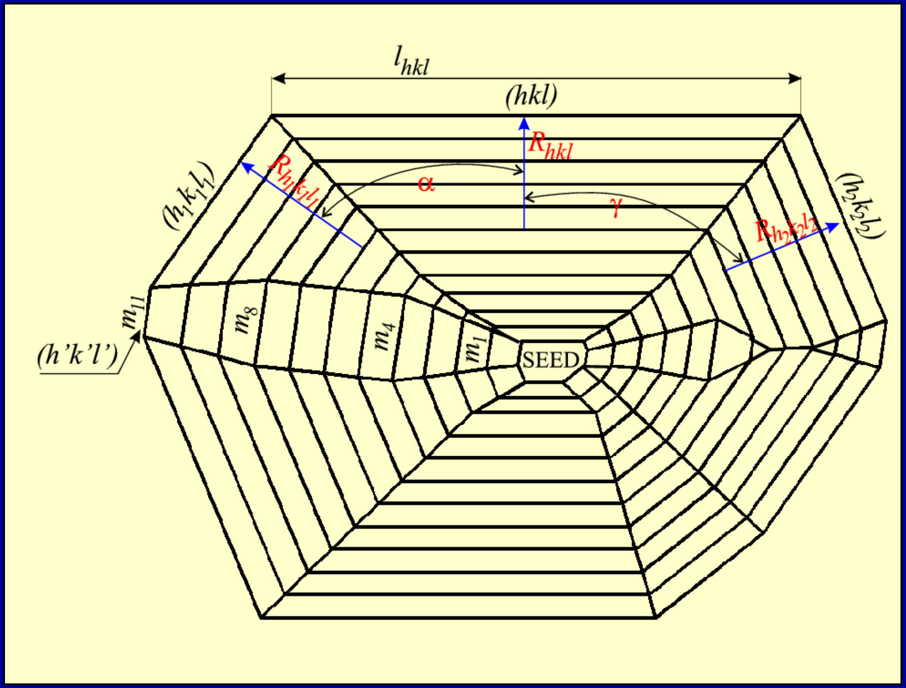
$$\frac{dl_{hkl}}{dt} = \frac{R_{h_1k_1l_1}sin(\gamma) + R_{h_2k_2l_2}sin(\alpha) - R_{hkl}sin(\alpha+\gamma)}{sin(\alpha)sin(\gamma)}$$

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

(i) $dl_{hkl}/dt > 0$ face (hkl) increases

(ii) $dl_{hkl}/dt = 0$ face (hkl) in not changed

(iii) $dl_{hkl}/dt > 0$ face (hkl) decreases

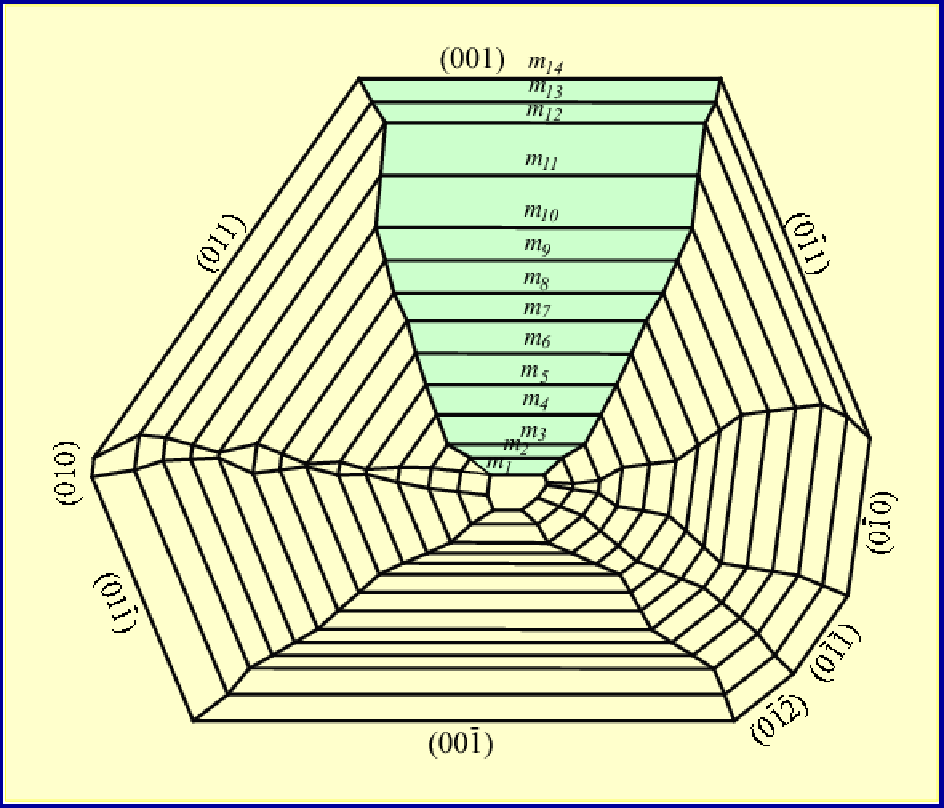


J. Prywer: "Crystal faces existence and morphological stability from crystallographic perspective" *Cryst. Growth Des.* **3** (2003) 593–598.

Morphological stability of the faces

$$face\ (001)$$
$$\alpha = 54.90\ arc\ deg, \gamma = 72.79\ arc\ deg$$

prążek	$\frac{R_{(001)}}{R_{(011)}}$	$\frac{R_{(001)}}{R_{(0\bar{1}1)}}$	$\frac{dl_{(001)}}{dt}$
0-1	0.52	0.46	4.63
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



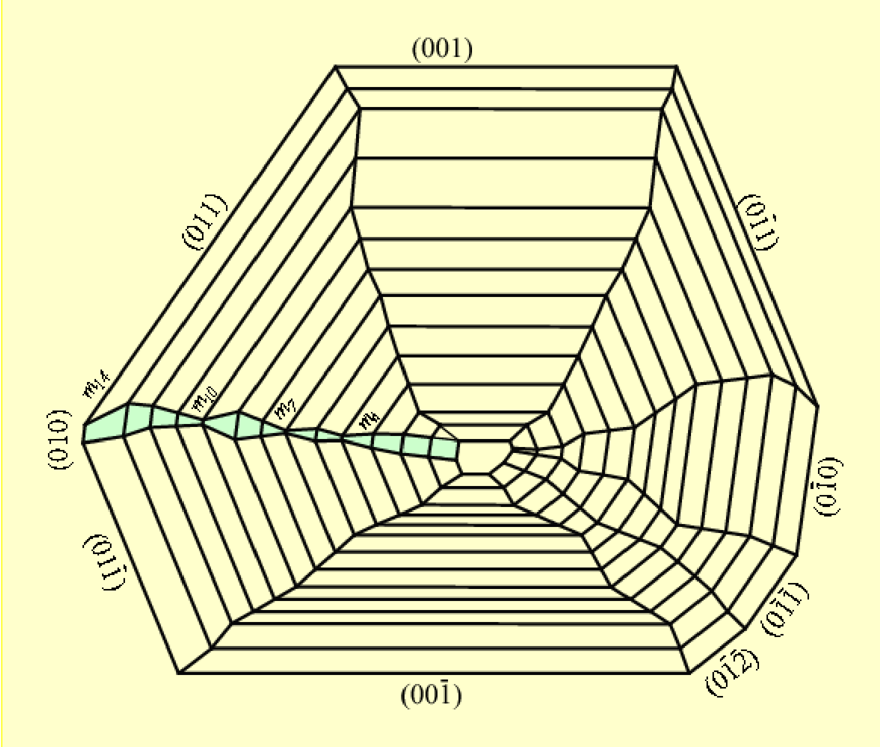
J. Prywer: "Crystal faces existence and morphological stability from crystallographic perspective" *Cryst. Growth Des.* **3** (2003) 593–598.

Morphological stability of the walls

Wall (010)

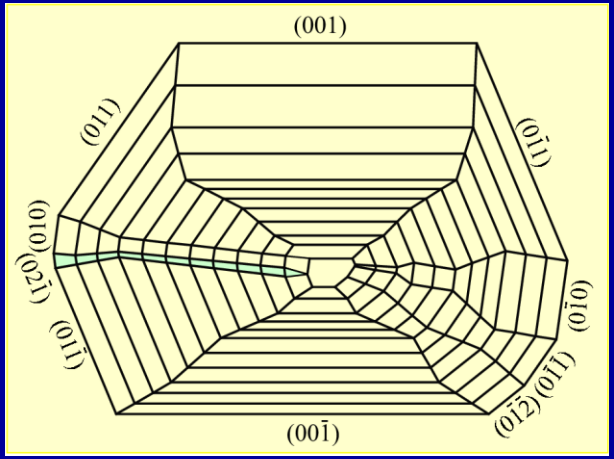
$\alpha = 30.80\ arc\ deg, \gamma = 27.01\ arc\ deg$

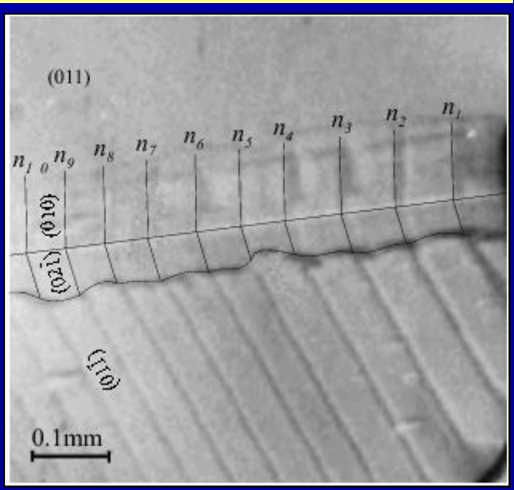
prążek	$\frac{R_{(010)}}{R_{(01\bar{1})}}$	$\frac{R_{(010)}}{R_{(011)}}$	$\frac{dl_{(010)}}{dt}$
0-1	1.00	0.72	2.47
1-2; 2-3	1.14	1.14	0.00
3-4	1.20	1.20	-0.42
4-5	1.25	1.25	-0.79
5-6	1.05	1.05	0.67
6-7	1.25	1.25	-0.79
7-8; 8-9	1.00	1.00	1.03
9-10	1.40	1.40	-1.88
10-11; 11-12	1.05	1.05	0.67
12-13	0.89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



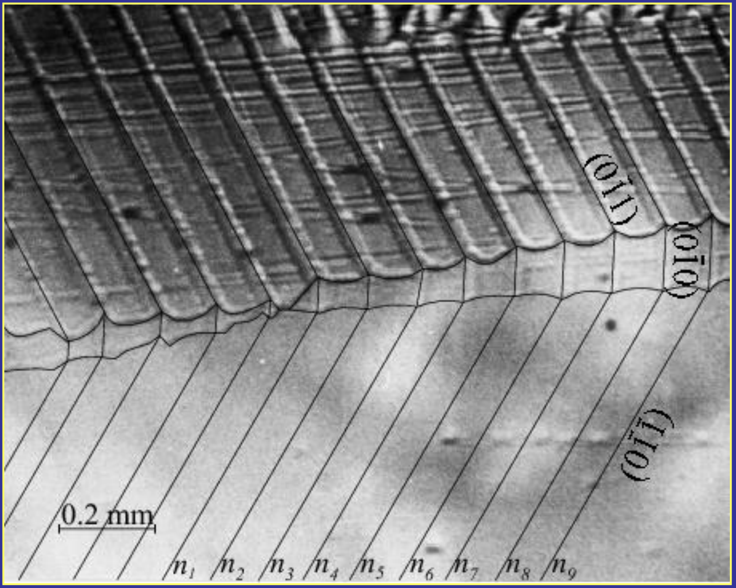


Face $(02\bar{1})$

$\alpha = 14.84\ arc\ deg, \gamma = 15.96\ arc\ deg$

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

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

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

MI (morphological importance)

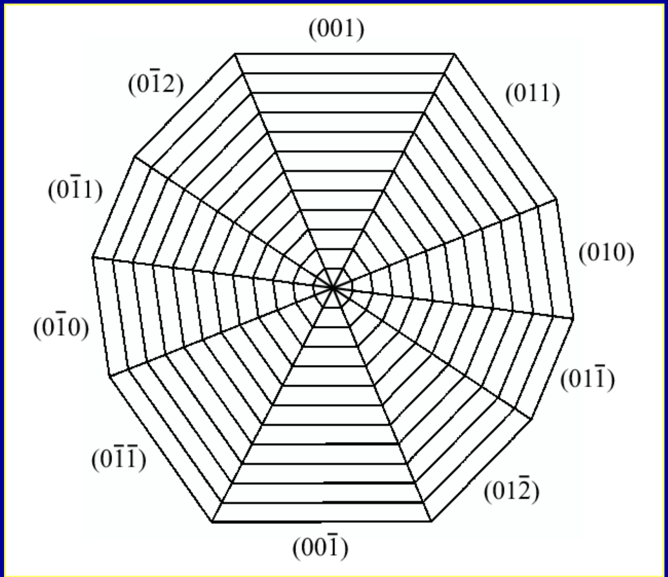
G. Friedel, *Leçon de Cristallographie*, Hermann, Paris (1911).

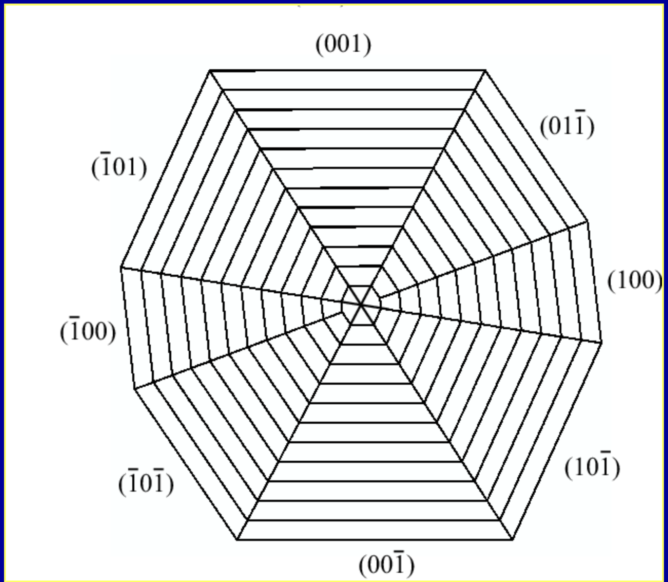
A. Bravais, *Études Cristallographiques*, Gauthier-Villard, Paris (1913).

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.

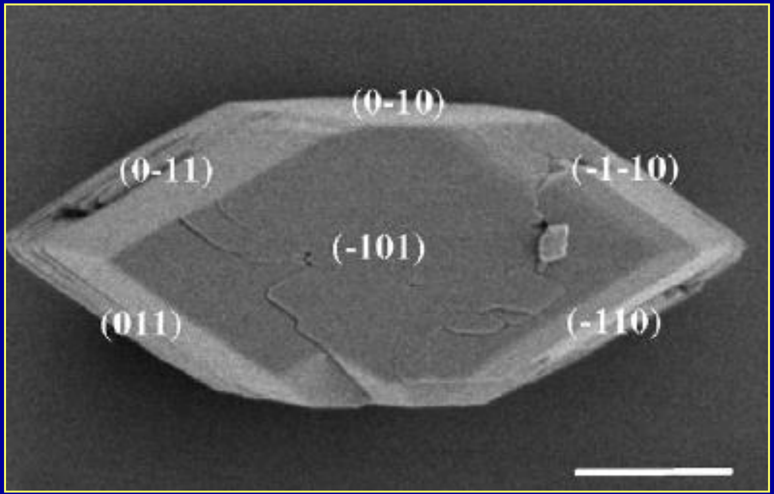
Growth rate rules

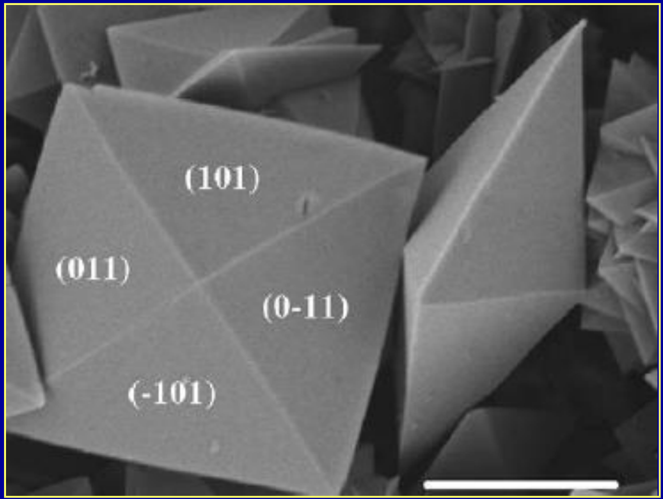
- **Attachment energy rule (Hartmann et al.)**

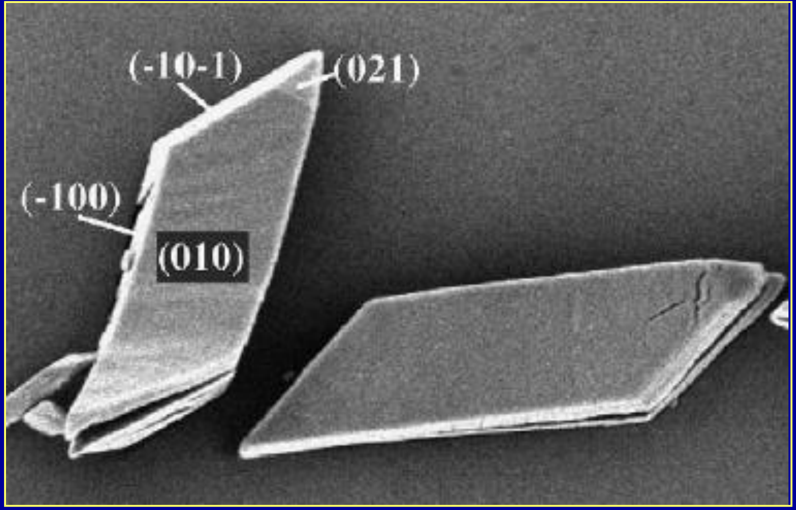
$$R_{hkl} \propto E_{hkl}$$

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

Calcium oxalate - $CaC_2O_4*(H_2O)_x$



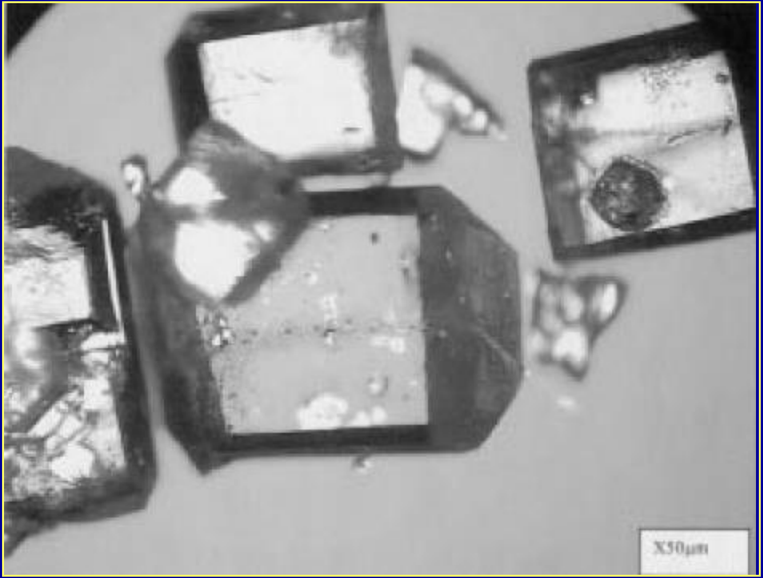




R. C. Waltion, J.P. Kavanagh, B. R. Heywoodb, P. N. Rao,
Calcium oxalates grown in human urine under different batch conditions.
J. Cryst. Growth 284 (2005) 517

Pharmaceutics

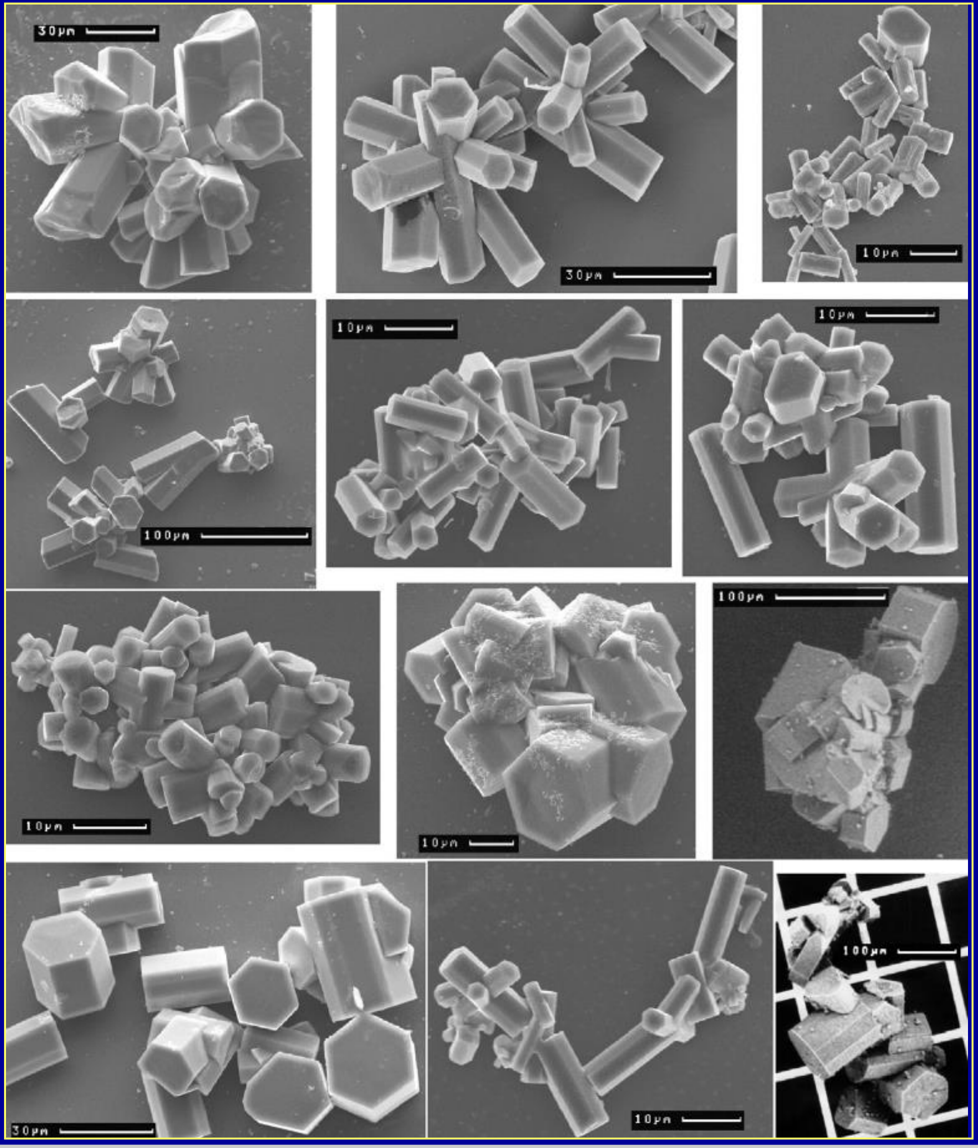
Ascorbic Acid – C_6H_8O



Vitamin C crystals grown from water solution by slow evaporation.

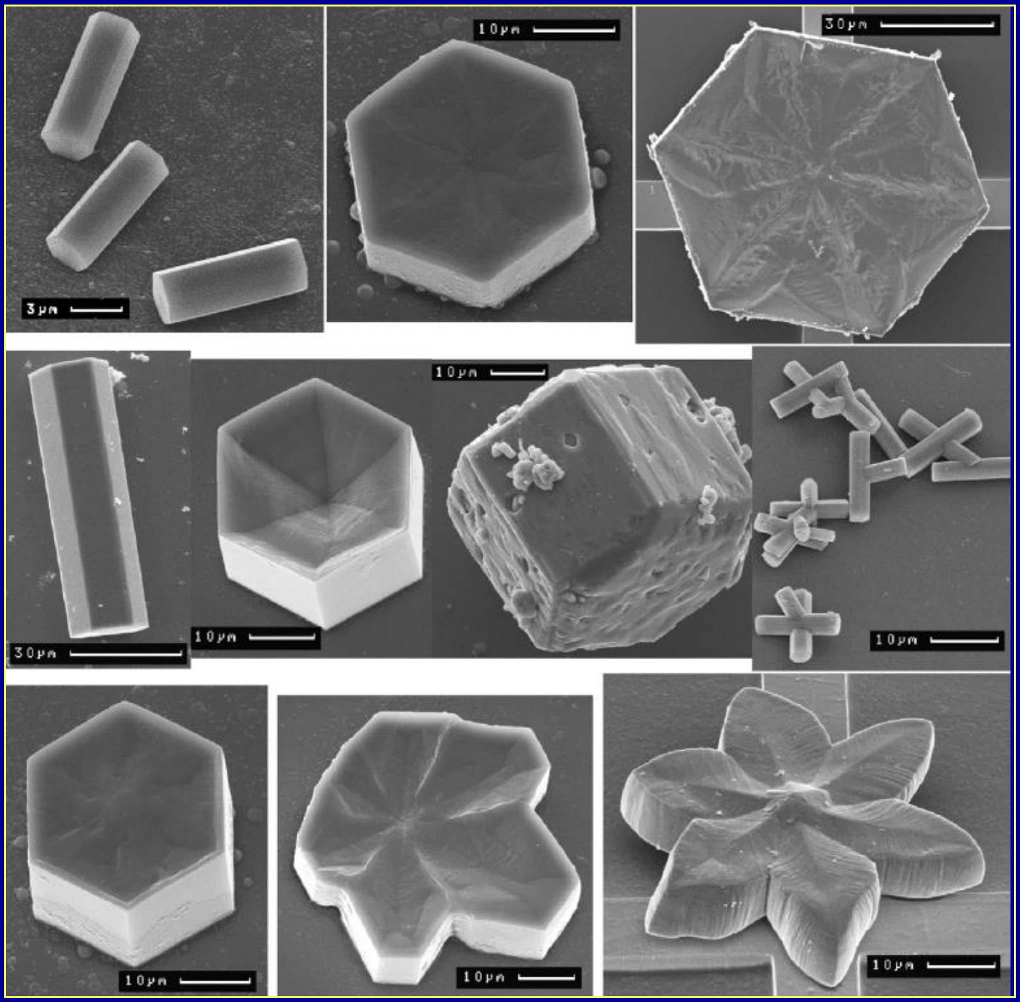
A. Arslants, W.C. Emler, R. Yazici, D. M. Kalyon, *Crystal Habit Modification of Vitamin C (L-Ascorbic Acid) due to Solvent Effects.* Turk. J. Chem. 28 (2004) 255

Na_2SiF_6 – crystal analogy to ice



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

Na_2SiF_6 – crystal analogy to ice



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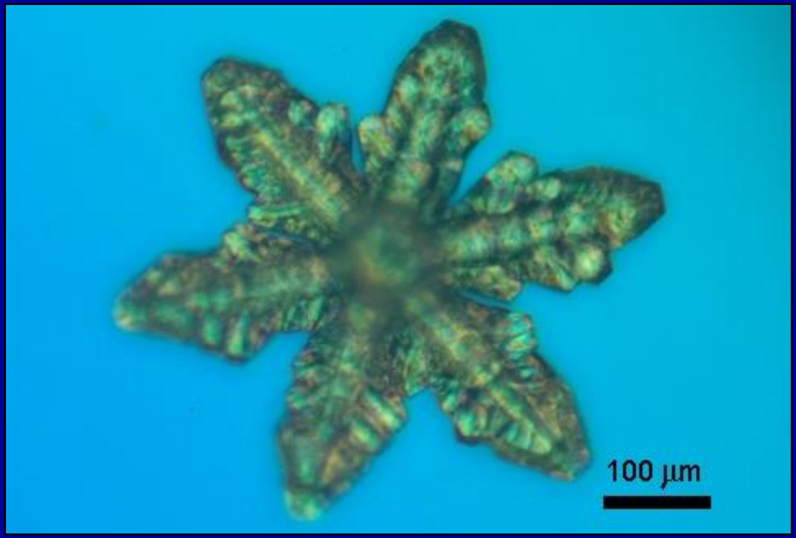
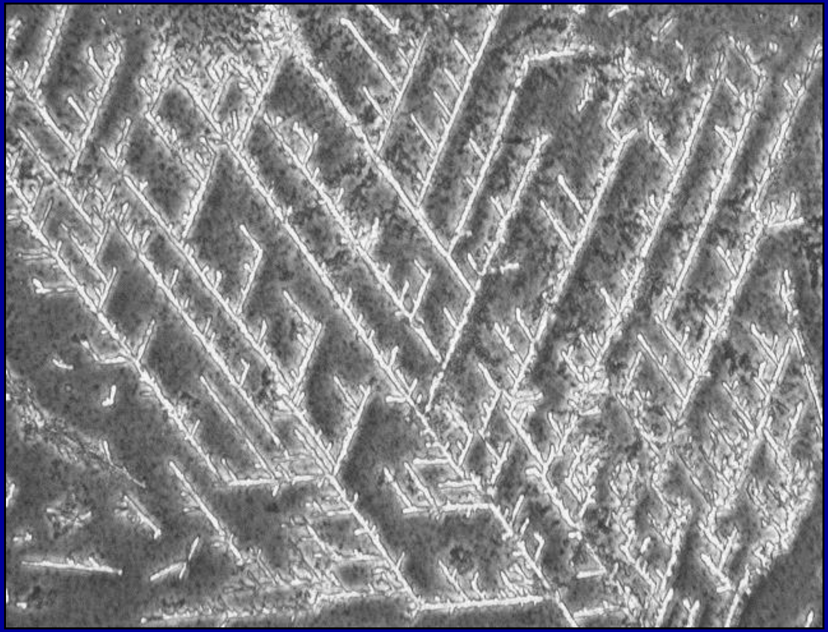
Na_2SiF_6 – crystal analogy to ice



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

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 mode:

- **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**

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

- **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

$$\lambda > 0 \quad unstable$$
$$\lambda < 0 \quad stable$$

Flat crystallization front – growth from solution

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

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

$$C_s = const(t)$$

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

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

- **Boundary conditions z = vt**

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

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

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

$$C_s = kC_l$$

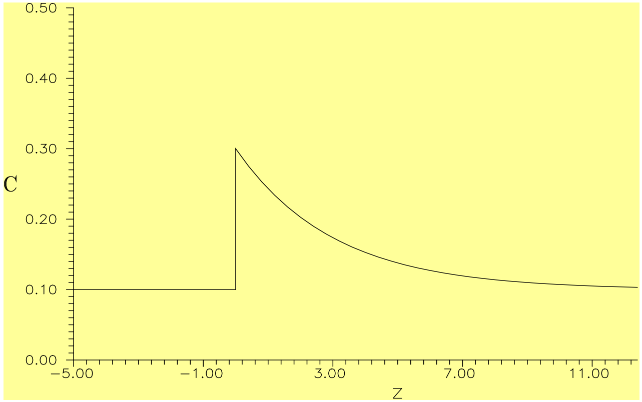
- **Solution – stationary in the interface coordination system**

Flat crystallization front

- **Concentration**

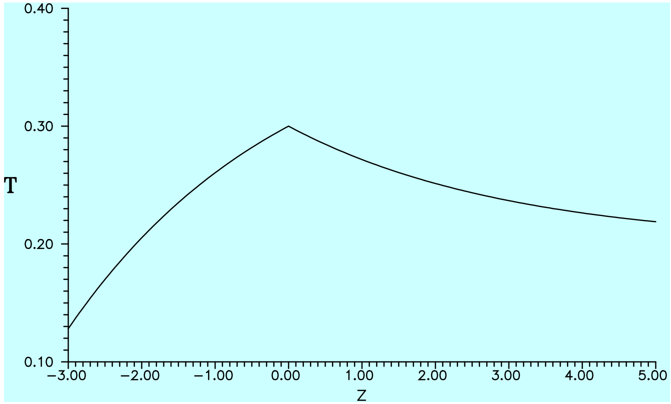
$$C_l = C_s + C_s \frac{1-k}{k} \exp\left[-\frac{vz}{D}\right] = C_s + \frac{GD}{v} \exp\left[-\frac{vz}{D}\right]$$

G – solute gradient at interface

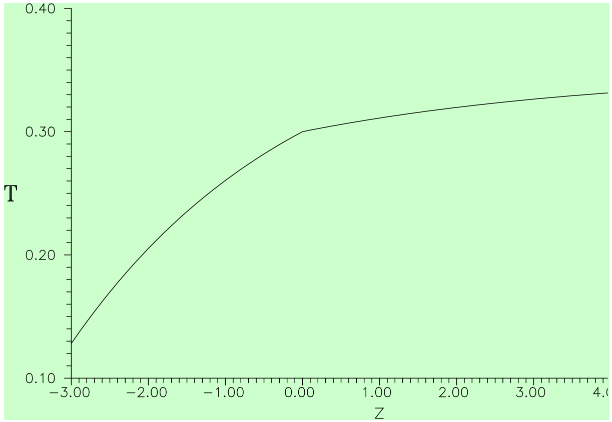


- **Temperature**

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



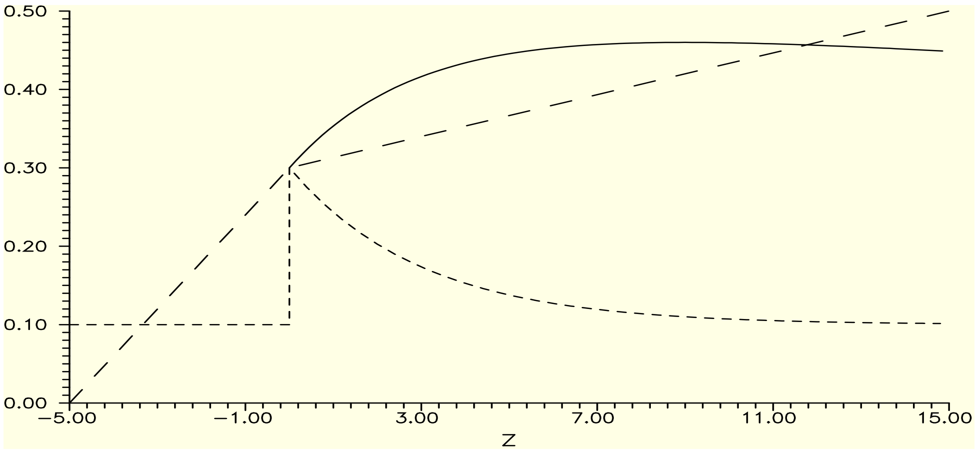
Liquid superooling $G_L < 0$



No liquid superooling $G_L > 0$

Constitutional supercooling at flat front

- **Effective melting temperature:** $\boldsymbol{T_1 = T_M + m\, C_l}$



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

- **Constitutive supercooling condition:** $\boldsymbol{G_l < m\, G}$

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

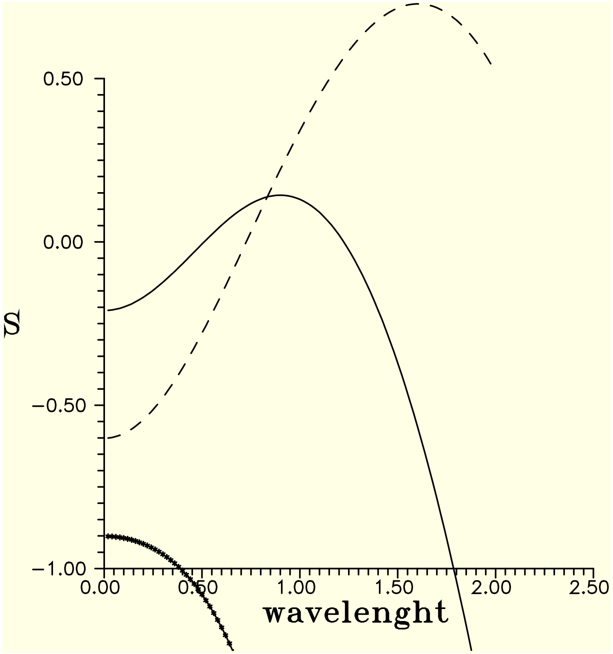
Mullins –Sekerka theory of morphological stability

- **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**

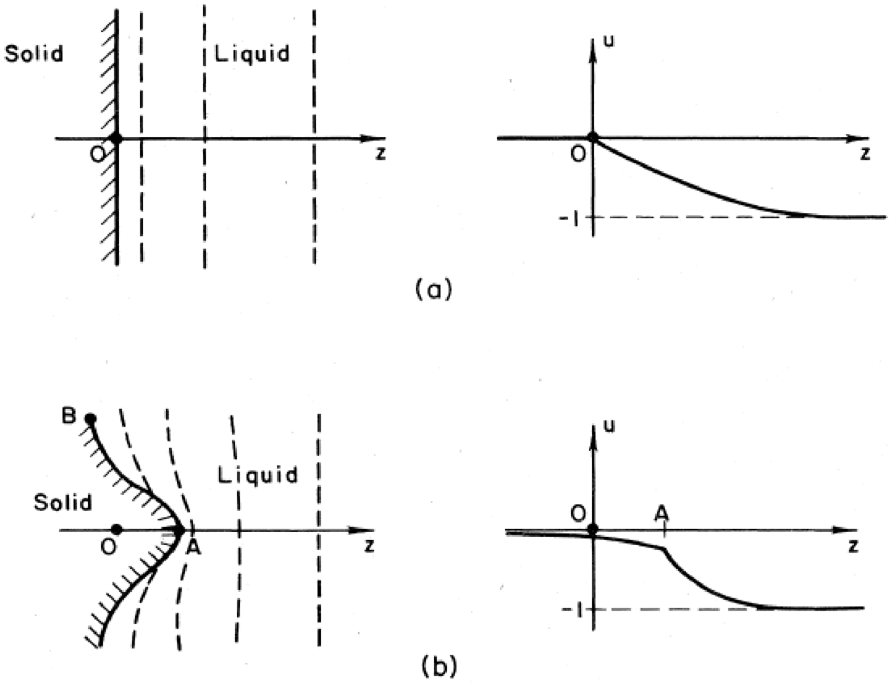
$$\lambda = \frac{v\omega\left\{(-2T_M\Gamma\omega^2 - G_l + G_s)\left[q + \frac{(1-k)v}{D}\right] - 2mG\left[q - \frac{v}{D}\right]\right\}}{(G_l - G_s)\left[q - \frac{(1-k)v}{D}\right] + 2kmG}$$

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

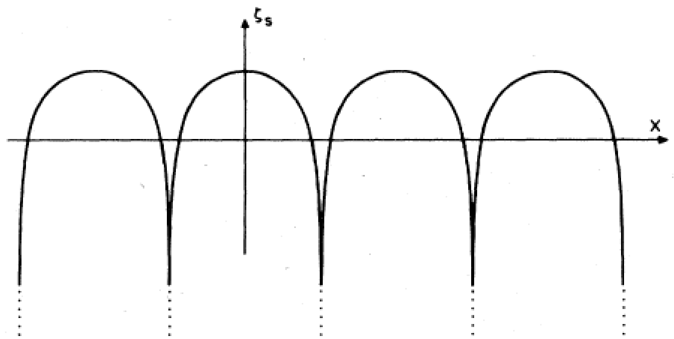
W.W. Mullins & R.F. Sekerka, J. Appl. Phys. 35 (1964) 444

Mullins –Sekerka instability of flat surface – cellular growth

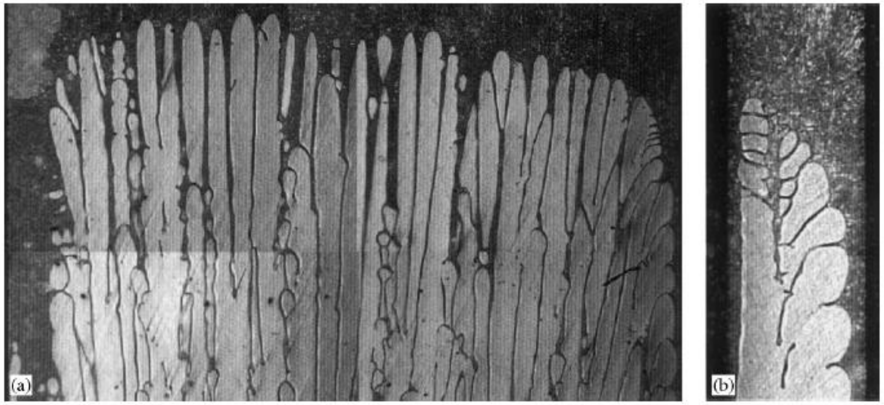
- **Instability mechanism**



- **Cellular interface**



- **Al.-4% Cu alloy**



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)

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

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

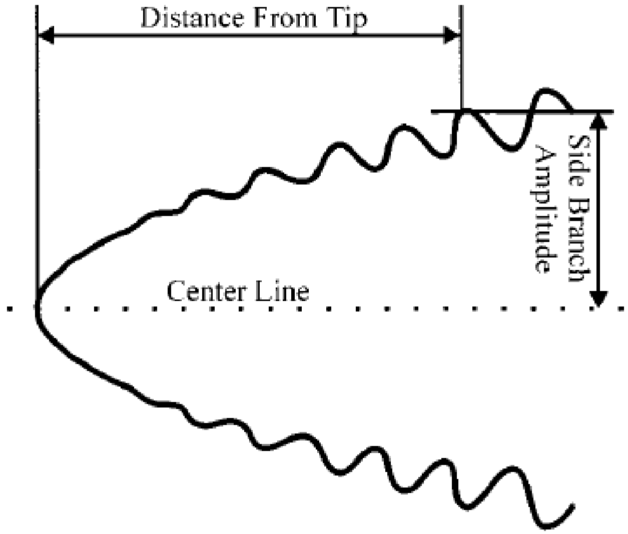
$R < 7R_{cr}$ $\lambda < 0$ **- stable**

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

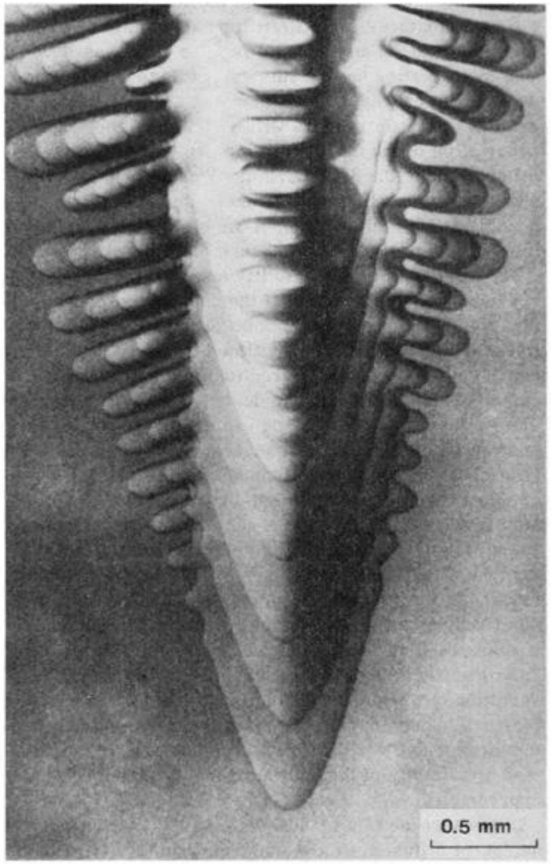
W.W. Mullins & R.F. Sekerka,J. Appl. Phys. 34 (1963) 323

Side instability – evolution of dendrite - sidebranching

Dendrite geometry – side has larger radius



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



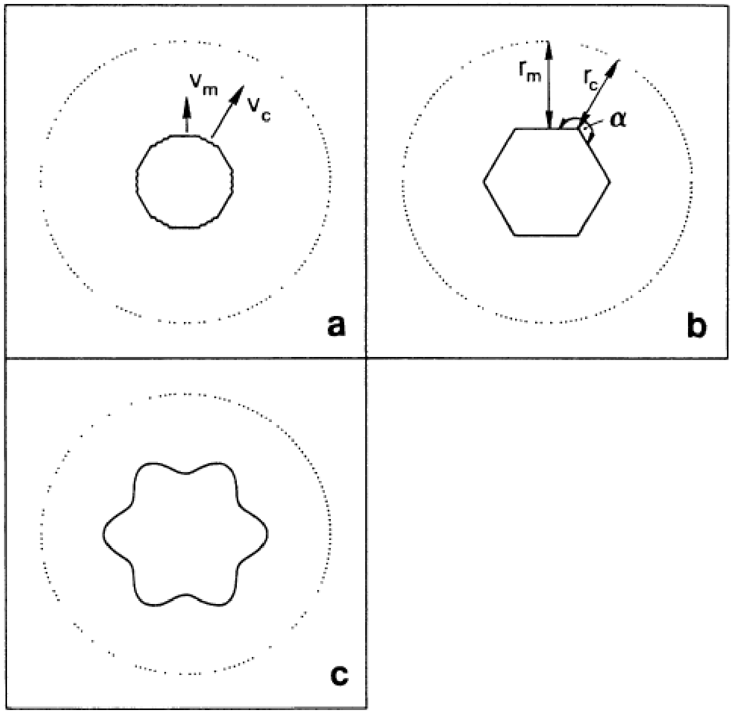
S.C. Huang & M.E. Glicksman,
Acta Metall. 29 (1981) 701

Edge instability in diffusion field

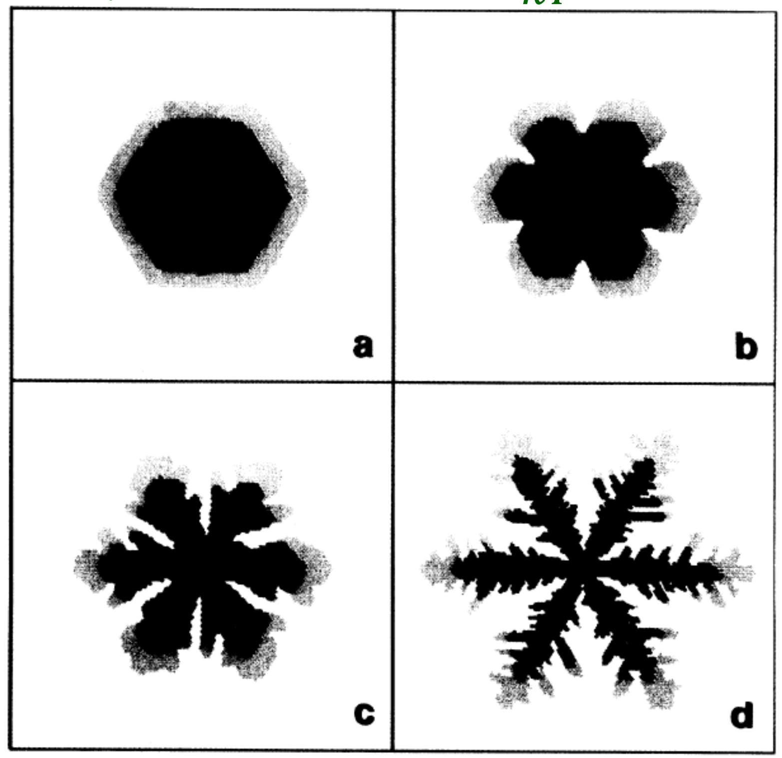
- **Polyhedral shape → Edge instability → Needle effect → Higher rate**

$\boldsymbol{\sigma = 0.69}$

Angular access



$\frac{\phi}{kT} = 3.91$ $\frac{\phi}{kT} = 2.3$



$\frac{\phi}{kT} = 0.69$ $\frac{\phi}{kT} = 0.36$

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

Edge instability in ballistic/diffusive transport field

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

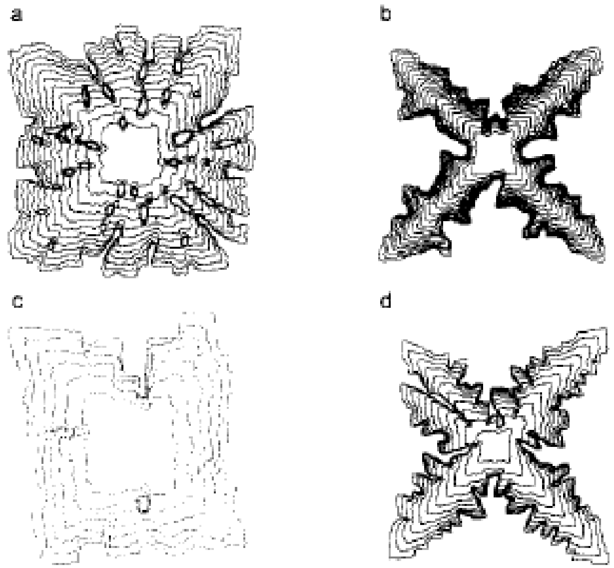
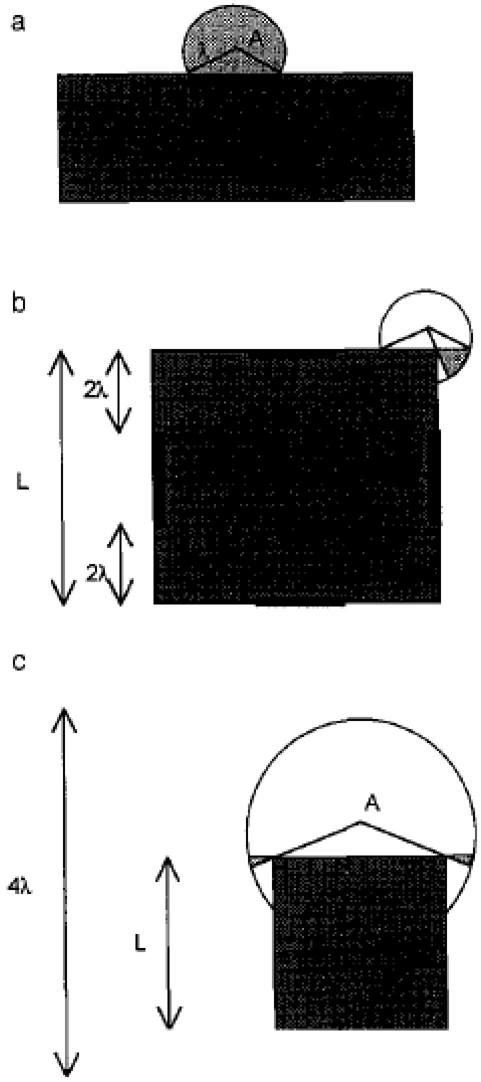


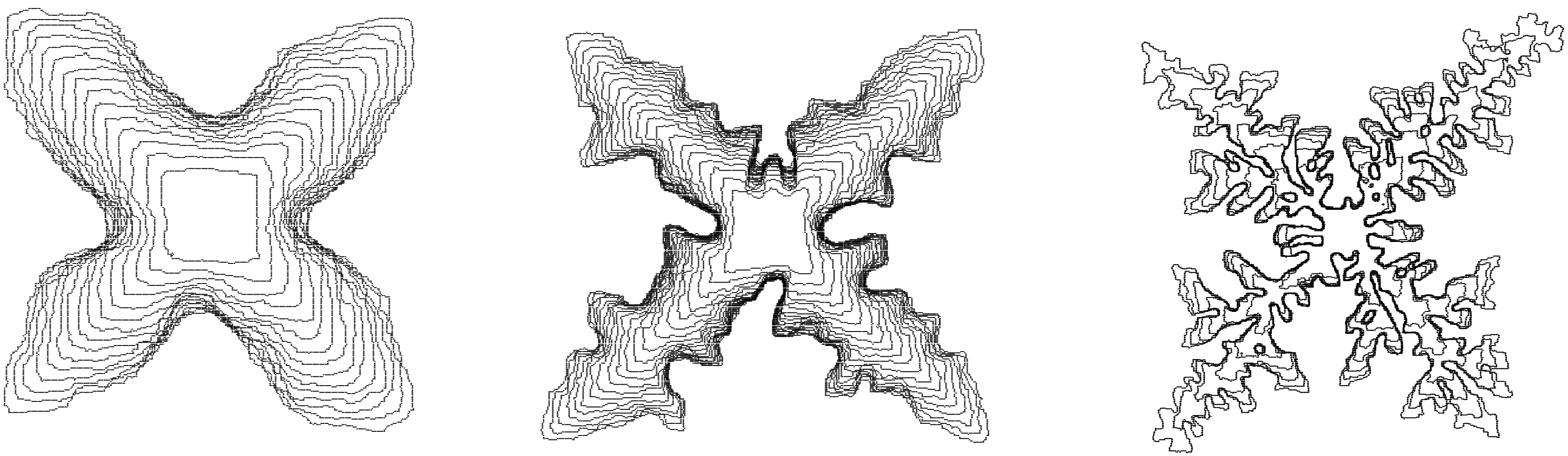
Fig. 7. Ballistic and diffusive transport modes: (a) $\lambda = 100a$; (b) $\lambda = 10a$, $L \approx 400a$; (c) $\lambda = 50a$, $L \approx 100a$; (d) $\lambda = 50a$, $L \approx 400a$. The other parameters are: $\epsilon = 6.0$, $\sigma = 1999$ and $\xi = 0.0$.



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

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

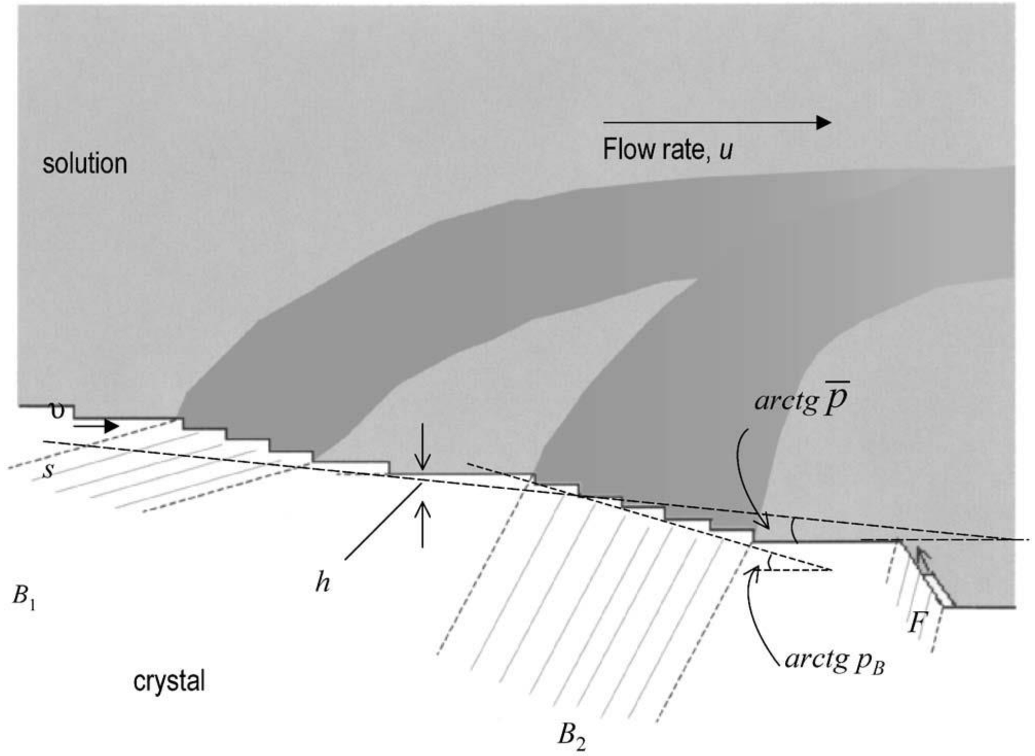




http://www.its.caltech.edu/~atomic/snowcrystals/photos/photos.htm

Microscopic scenario of instability

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



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