2018 Fall

Advanced Solidification

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Contents for previous class

- **Undercooling ΔT**
- **Interfacial energy**
  γ_{SL} / S(θ) wetting angle

Solidification: Liquid ⟶ Solid

< Nucleation in Pure Metals>

* Homogeneous Nucleation

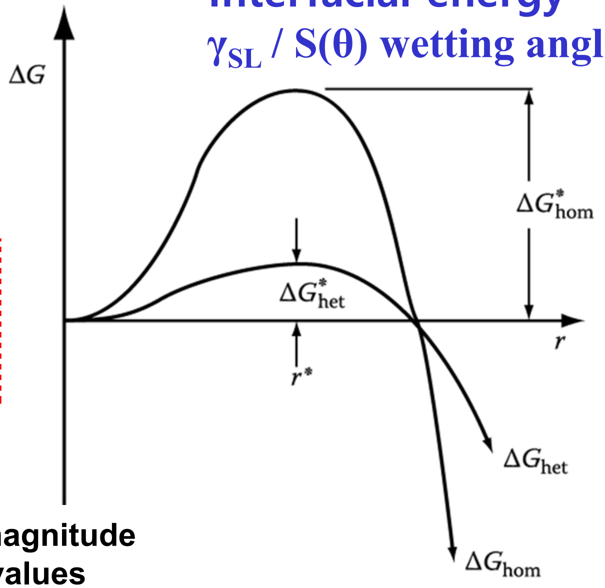
$$r^* = \frac{2\gamma_{SL}}{\Delta G_V}$$

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_V)^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2}\right)\frac{1}{(\Delta T)^2}$$

r* & ΔG* ↓ as ΔT ↑

$$N_{\text{hom}} \approx f_0 C_o \exp\{-\frac{A}{(\Delta T)^2}\}$$

changes by orders of magnitude from zero to very high values over a very narrow temp. range



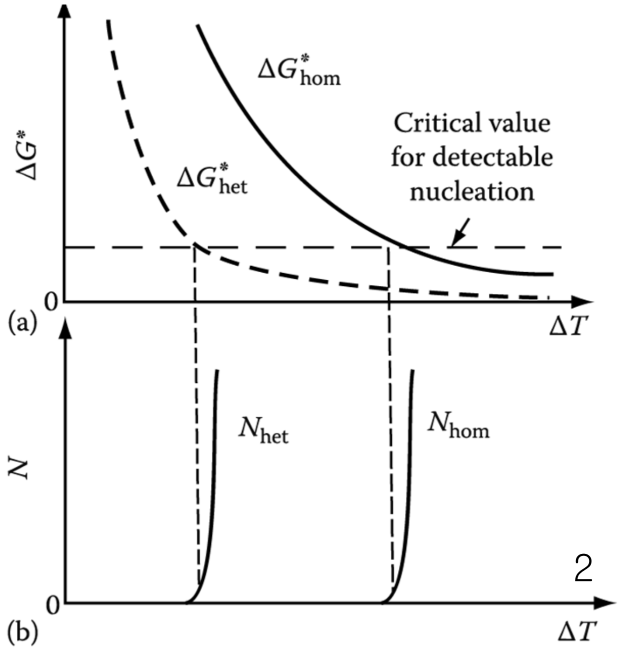
* Heterogeneous Nucleation

$$\Delta G^*_{het} = S(\theta)\Delta G^*_{\text{hom}}$$

$$\frac{V_A}{V_A + V_B} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = S(\theta)$$

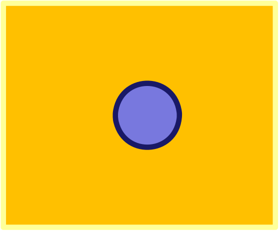
* Nucleation of melting

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$ **(commonly)**



Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



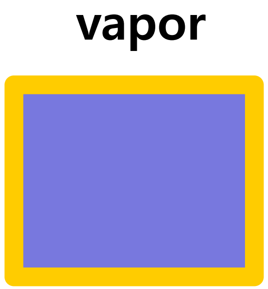
<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

No superheating required!

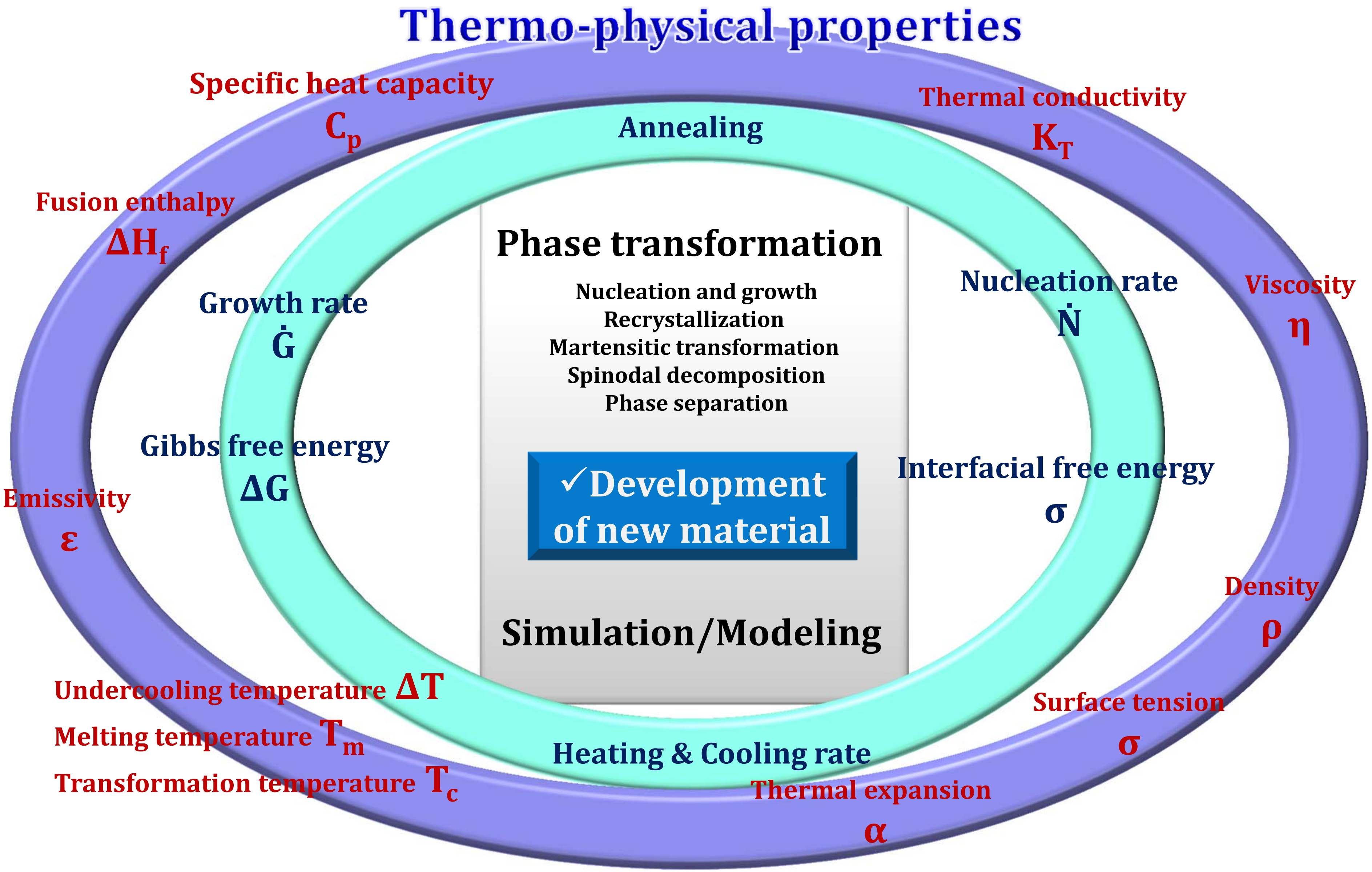
- Interfacial energy ⇨ No ΔT_N

$$\boxed{\gamma_{SL} + \gamma_{LV} < \gamma_{SV}}$$



Melting: Liquid ← Solid

Development of extreme condition endurance materials



Thermo-physical properties

Specific heat capacity C_p

Thermal conductivity K_T

Fusion enthalpy ΔH_f

Viscosity η

Emissivity ε

Density ρ

Surface tension σ

Undercooling temperature ΔT

Melting temperature T_m

Transformation temperature T_c

Thermal expansion α

Annealing

Growth rate $\dot{G}$

Nucleation rate $\dot{N}$

Gibbs free energy ΔG

Interfacial free energy σ

Heating & Cooling rate

Phase transformation

Nucleation and growth
Recrystallization
Martensitic transformation
Spinodal decomposition
Phase separation

✓Development of new material

Simulation/Modeling

Nucleation

**** Homogeneous Nucleation of crystal in supercooled liquid***

→ Well-defined by Turnbull and his coworker theoretically / experimentally.

**** Heterogeneous Nucleation***

→ detailed theory ~ less satisfactory

Nucleation ~ a function of the temperature in liquids that are not in motion

but In practice, liquids are often exposed to dynamic conditions.

< Two main type of dynamically stimulated nucleation >

1) completely metastable supercooled liquid containing no crystal
   → Nucleation by friction, ultrasonic vibration, pressure pulse , etc.

2) A phenomenon that the # of crystals is greatly increased by dynamic methods in solidifying liquid → It is difficult to conclude that it is not due to the fragmentation of pre-existing crystals.

**** Dynamically Stimulated Nucleation***

→ very poor understood

Chapter 1: Equilibrium consideration (Thermodynamics)

Chapter 2: Atomic mechanism (Kinetics)

Chapter 3. Nucleation

Chapter 4. Microscopic Heat Flow Considerations

Q: Heat Flow and Interface Stability

1) Superheated liquid

: Extraction of latent heat by conduction in the crystal

2) Supercooled liquid

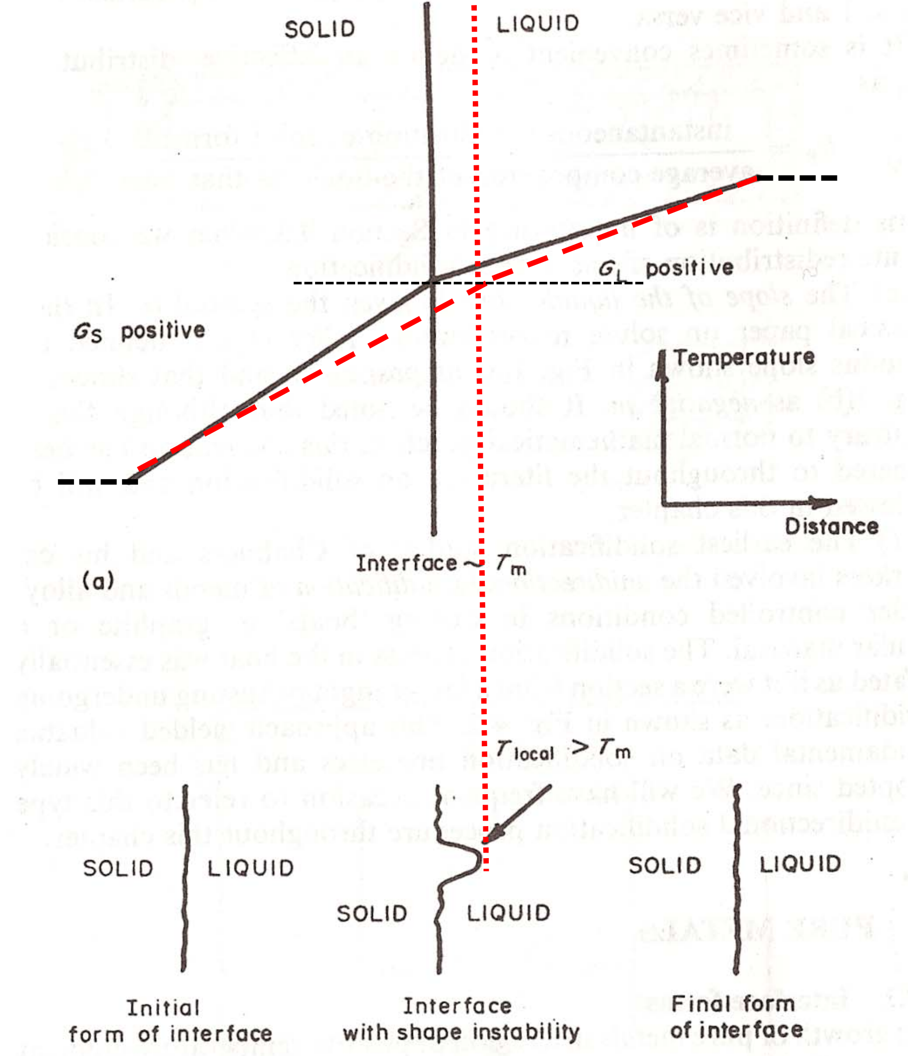
: conduction of latent heat into the liquid

→ **Development of Thermal Dendrite**

“Removal of latent heat” → Heat Flow and Interface Stability

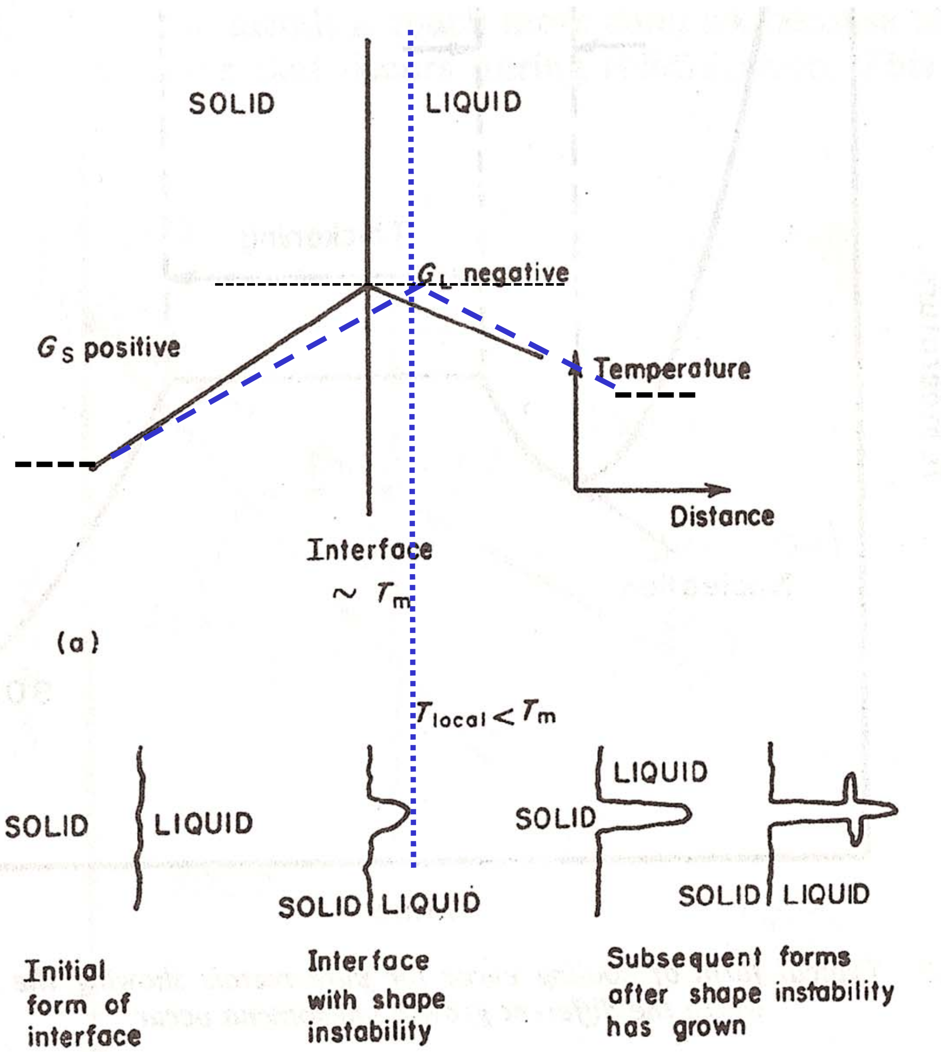
1) Superheated liquid

: Extraction of latent heat by conduction in the crystal



2) Supercooled liquid

: conduction of latent heat into the liquid

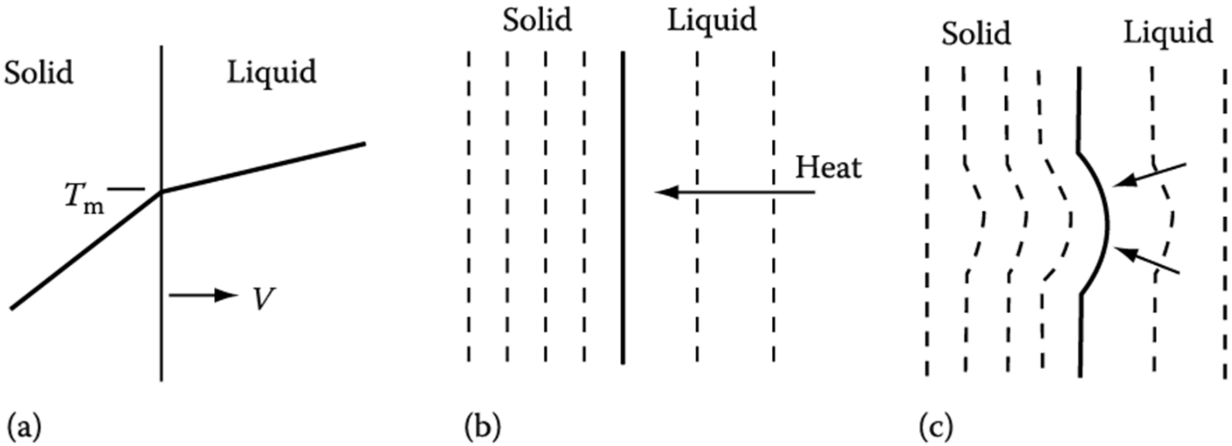


Heat Flow and Interface Stability - Planar interface

1) Superheated liquid: Extraction of Latent Heat by Conduction into the Crystal

Consider the solidification front with heat flow from L to S.

solid growing at *v*
(planar)



Heat flow away from the interface through the solid $K_S T'$

$K_L T_L'$ **- Heat flow from the liquid**

vL_V **- Latent heat generated at the interface**

Heat Balance Equation

$$K_S T_S' = K_L T_L' + vL_V$$

K: thermal conductivity

If r is so large → Gibbs-Thompson effect can be ignored the solid/liquid interface remain at T_m
(r : radius of curvature of the protrusion)

dT/dx in the liquid ahead of the protrusion will increase more positively. $T_L'\uparrow$ & $T_S'\downarrow$

More heat to the protrusion → melt away

***v* of protrusion ↓ to match other *v* in planar region**

mould walls

Single Crystal Growth: a) Czochralski Growing System

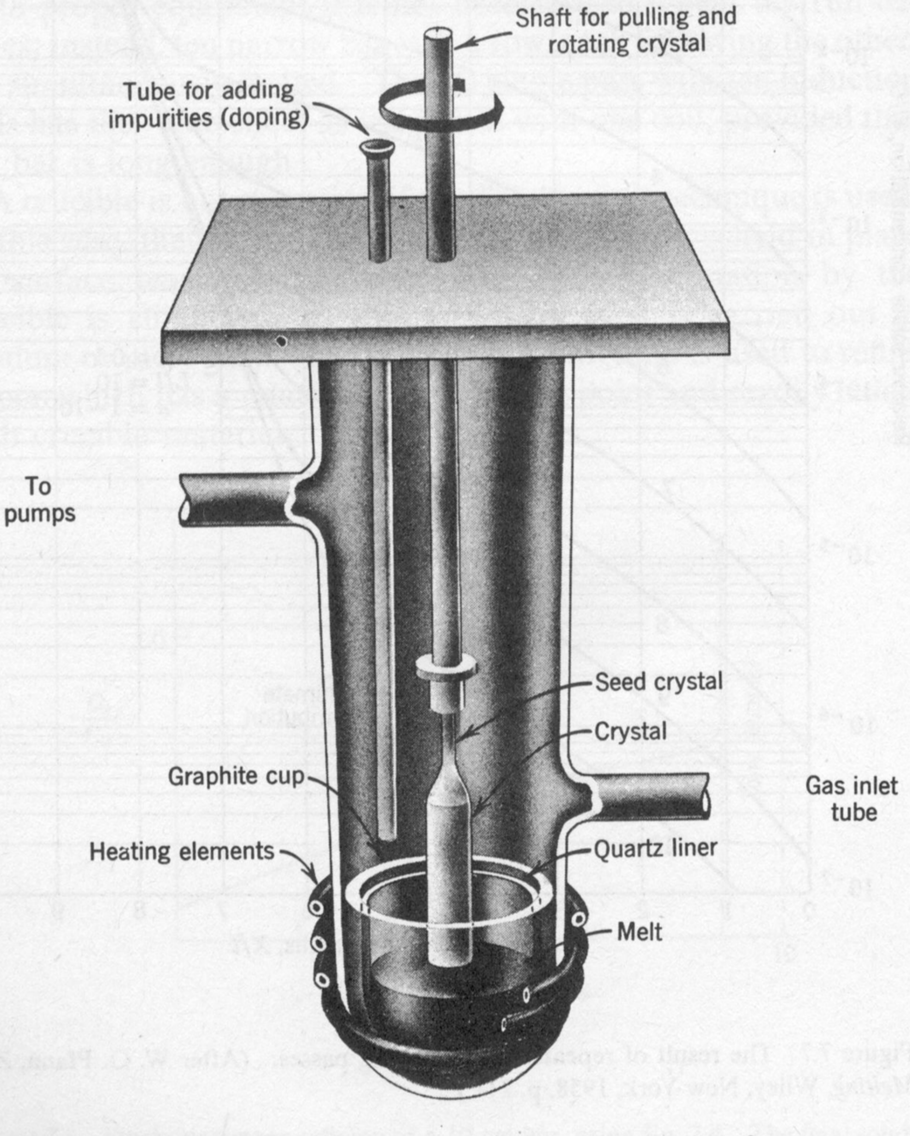
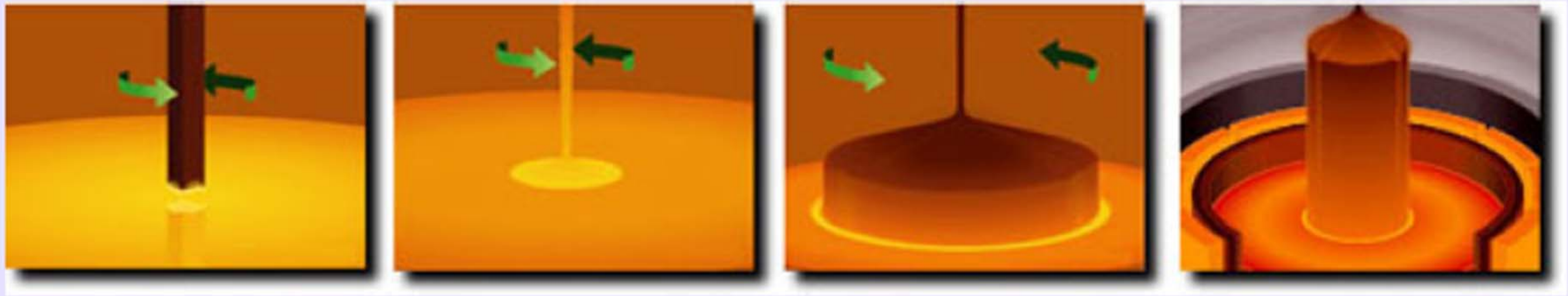
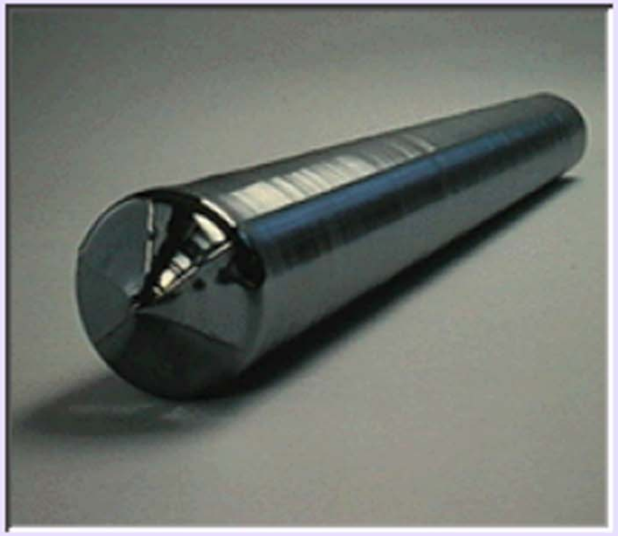


Figure 7.8 Schematic of a Czochralski crystal-pulling furnace.

Single Crystal Growth: a) Czochralski Growing System



“Pulls”boule out of the melt



Growth speed is 1–2 mm/min

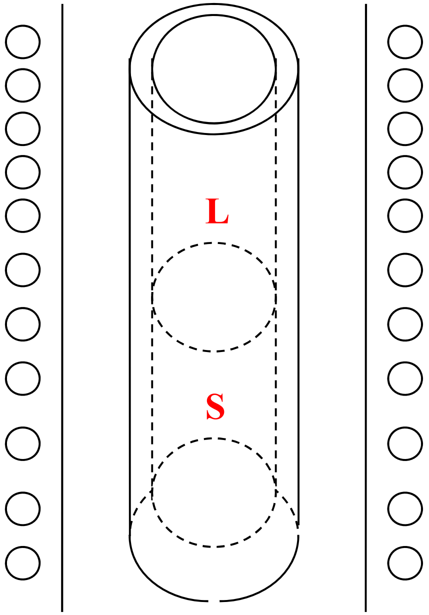
Czochralski(CZ) typically used for Si

Single Crystal Growth: b) Bridgman Technique

; Horizontal and vertical-type method

* The pointed end is first melted and slowly pulled from the inside of the furnace.

→ The pointed end first nucleates and grows into the crystal to become a single crystal.



Vertical

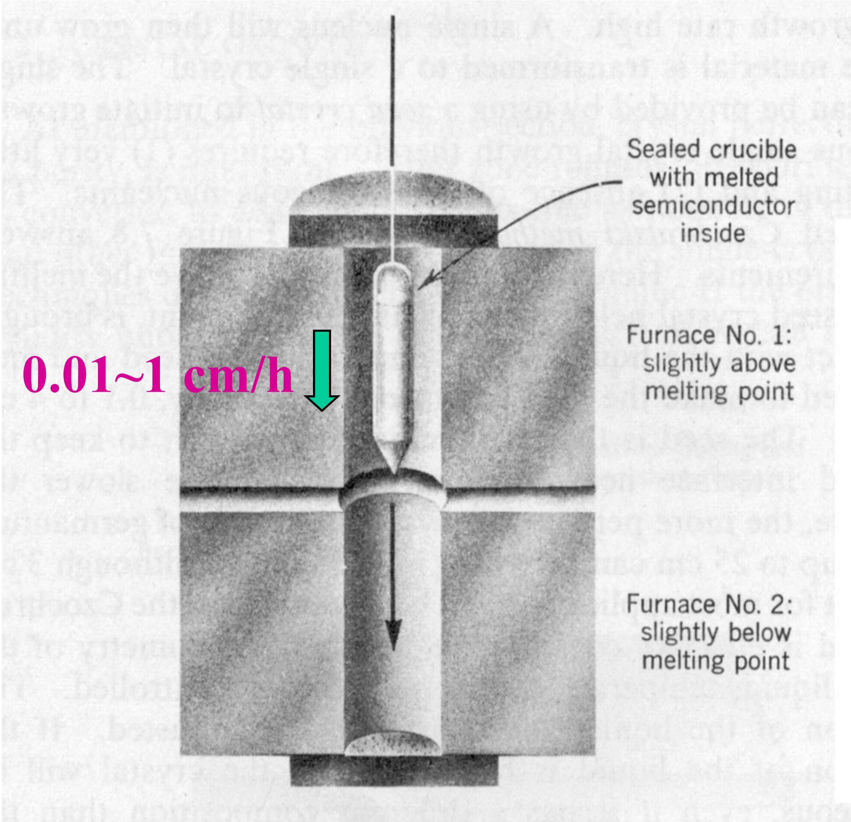
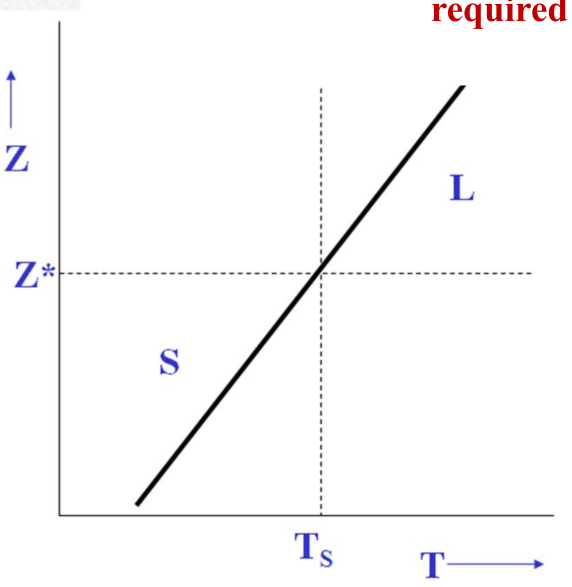


Figure 7.9 Schematic of Bridgman-Stockbarger crystal-growing apparatus.

Precise temperature gradient required



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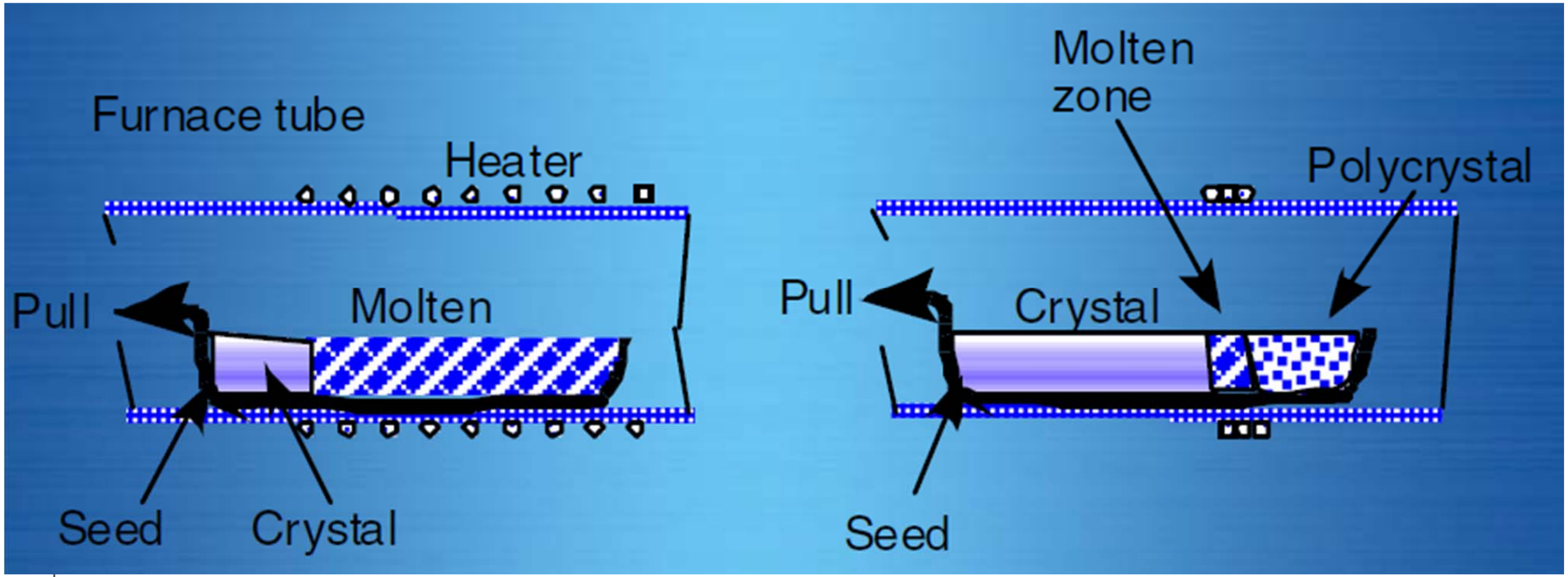
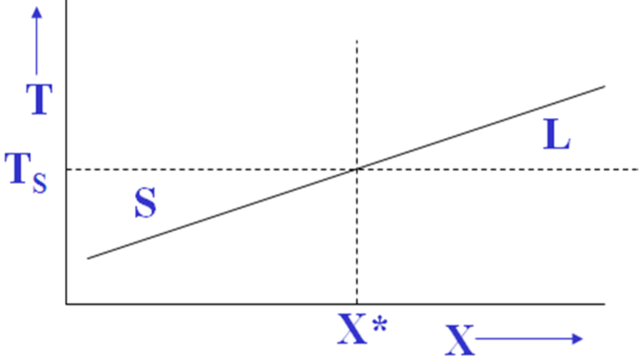
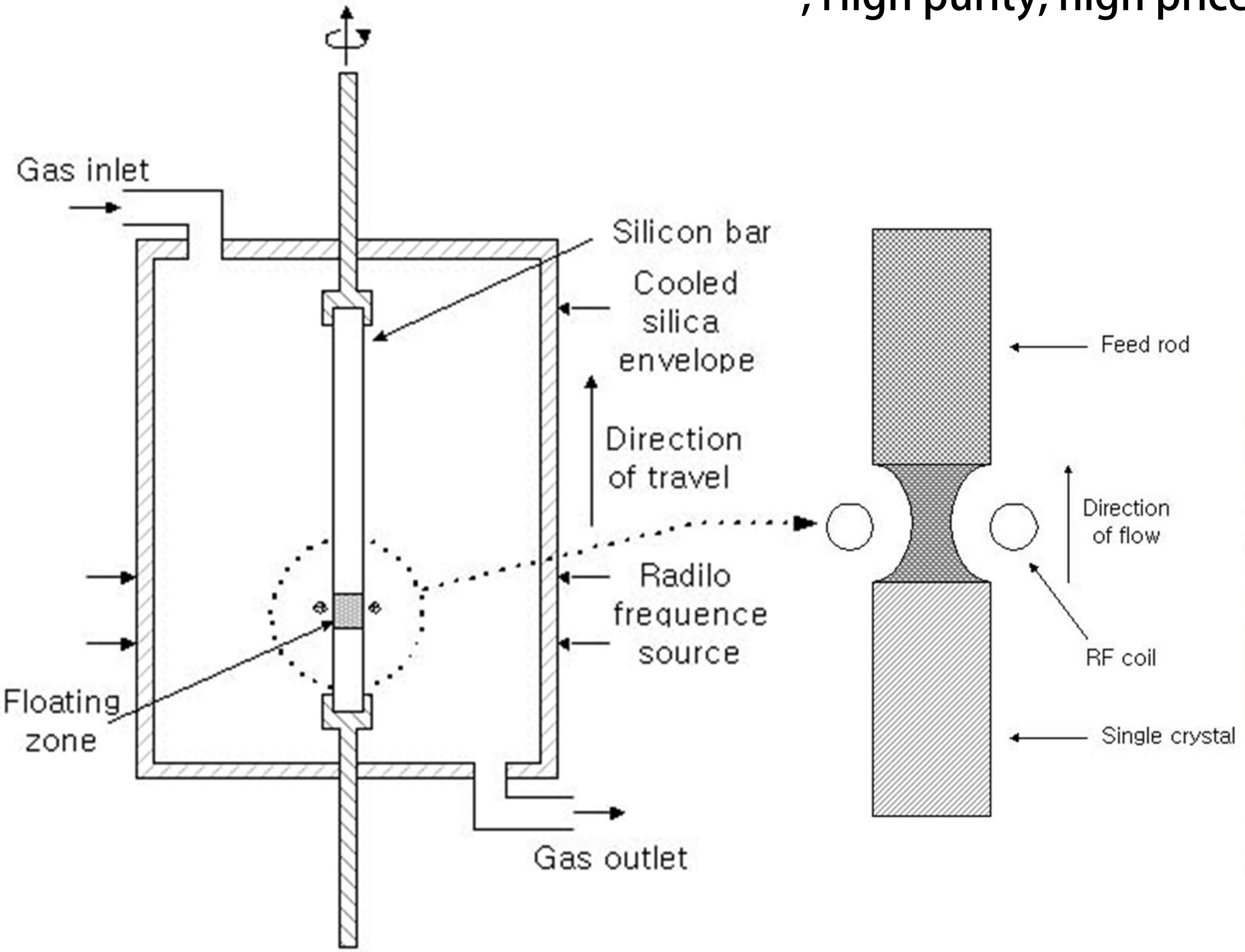




Carefully controlled temperature gradient required

Single Crystal Growth: c) Float-zone (FZ) method

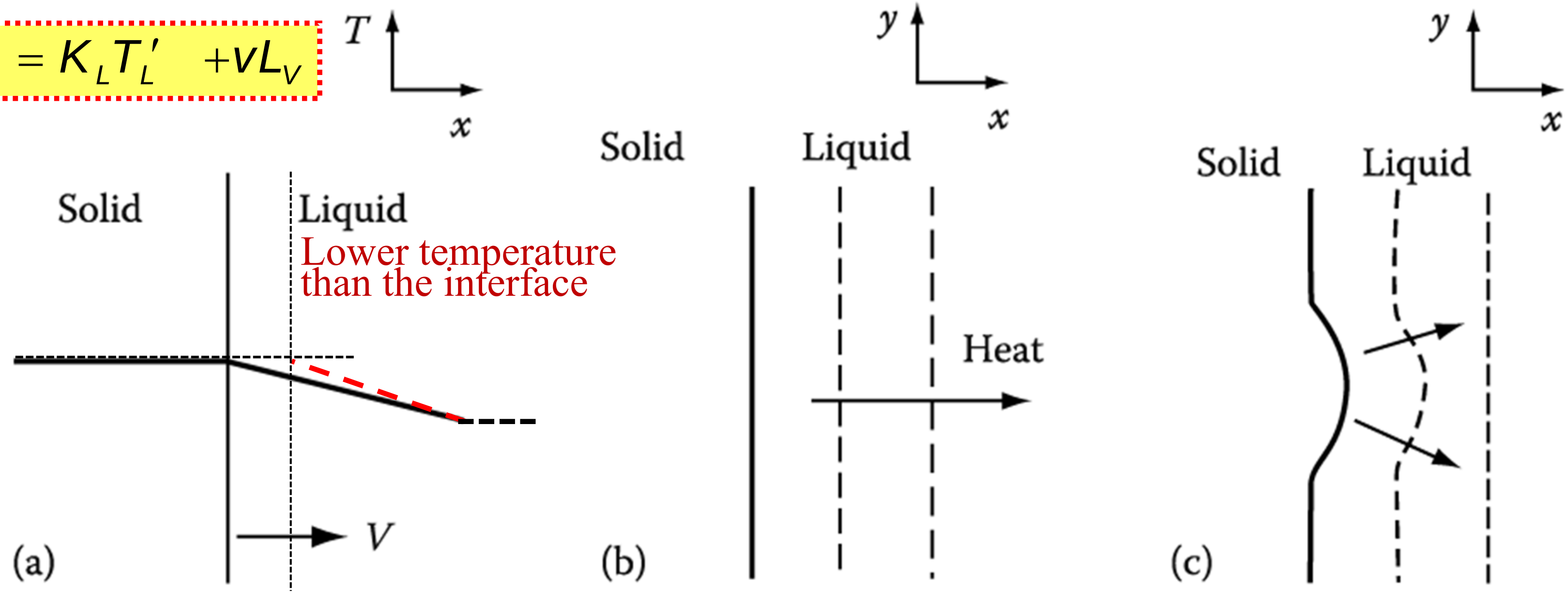
; High purity, high price.



Heat Flow and Interface Stability - Planar interface

2) Solid growing into SCL: conduction of latent heat into the liquid

$$K_S T_S' = K_L T_L' + vL_V$$



(a) Dendritic growth take place when, and only when, **the melt is supercooled**.

(b) Growth would be relatively slower near the plane, because the supercooling would be less there.

(c) The directions of growth are always strictly crystallographic.

(d) Branching occurs at roughly regular spacing, smaller for each successive order of branching.

- protrusion $\frac{dT_L'}{dX} < 0$ **becomes more negative**

→ heat flow from solid = the protrusion grows preferentially.

The earlier metallo-graphers believed that metals characteristically solidified in the dendritic form first described in detail by Tschernoff, who reproduced drawings of dendrites in 1868.

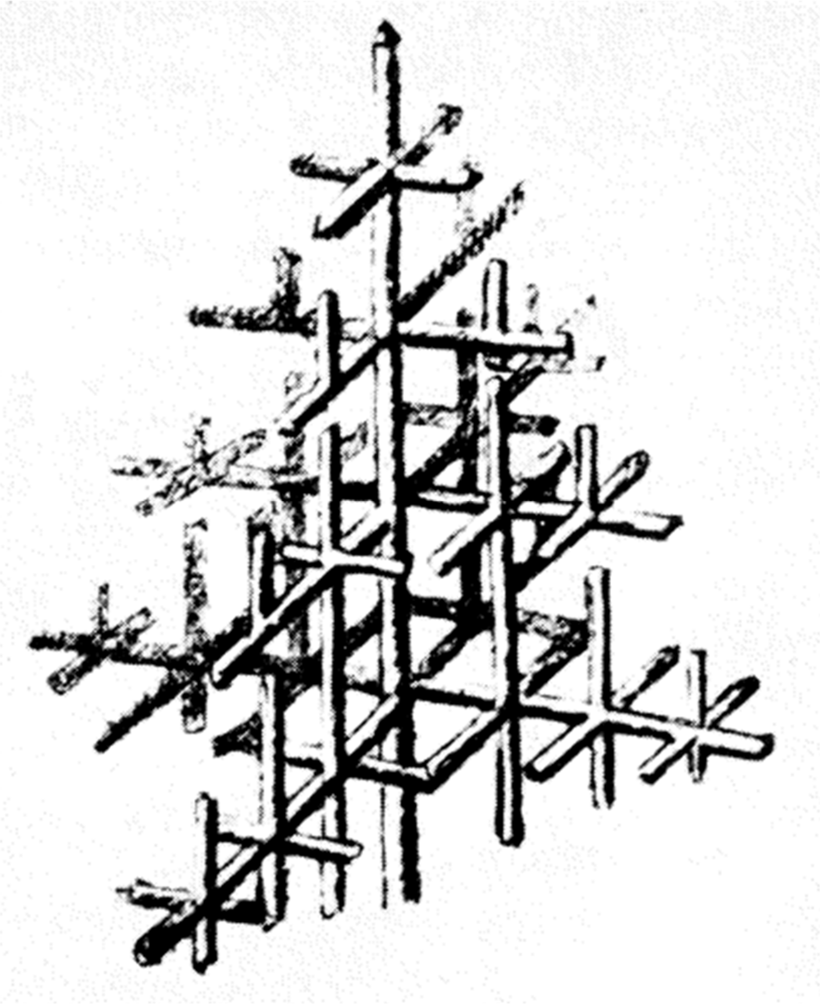


Fig. 4.1. Tschernoff's drawing of a dendrite. Reproduced from C. S. Smith, *A History of Metallography*, by permission of the Univ. of Chicago Press.

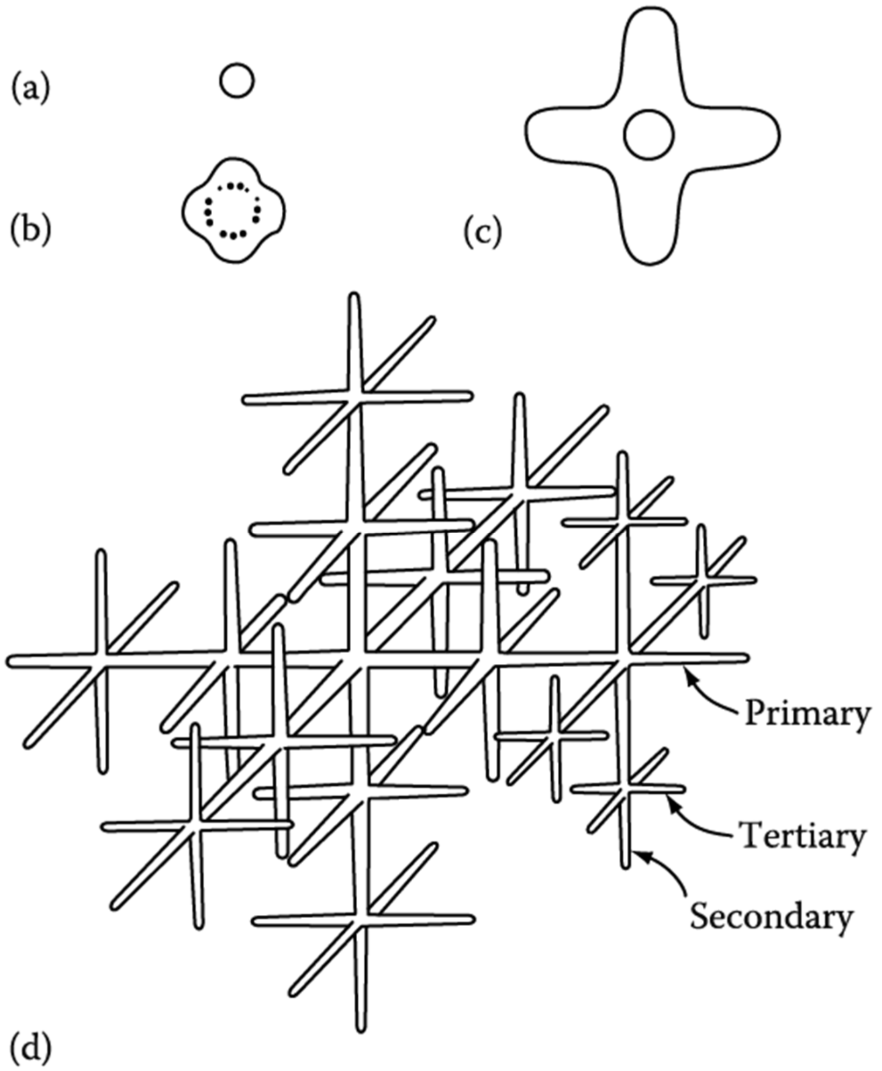
Development of Thermal Dendrite

cf) constitutional supercooling

When does heat flow into liquid?

→ Liquid should be supercooled below T_m.

→ Nucleation at impurity particles in the bulk of the liquid



The development of thermal dendrites: (a) a spherical nucleus; (b) the interface becomes unstable; (c) primary arms develop in crystallographic directions (<100> in cubic crystals); (d) secondary and tertiary arms develop

If the furnace is removed and the liquid loses heat fast enough to become supercooled, then dendritic solidification takes place.

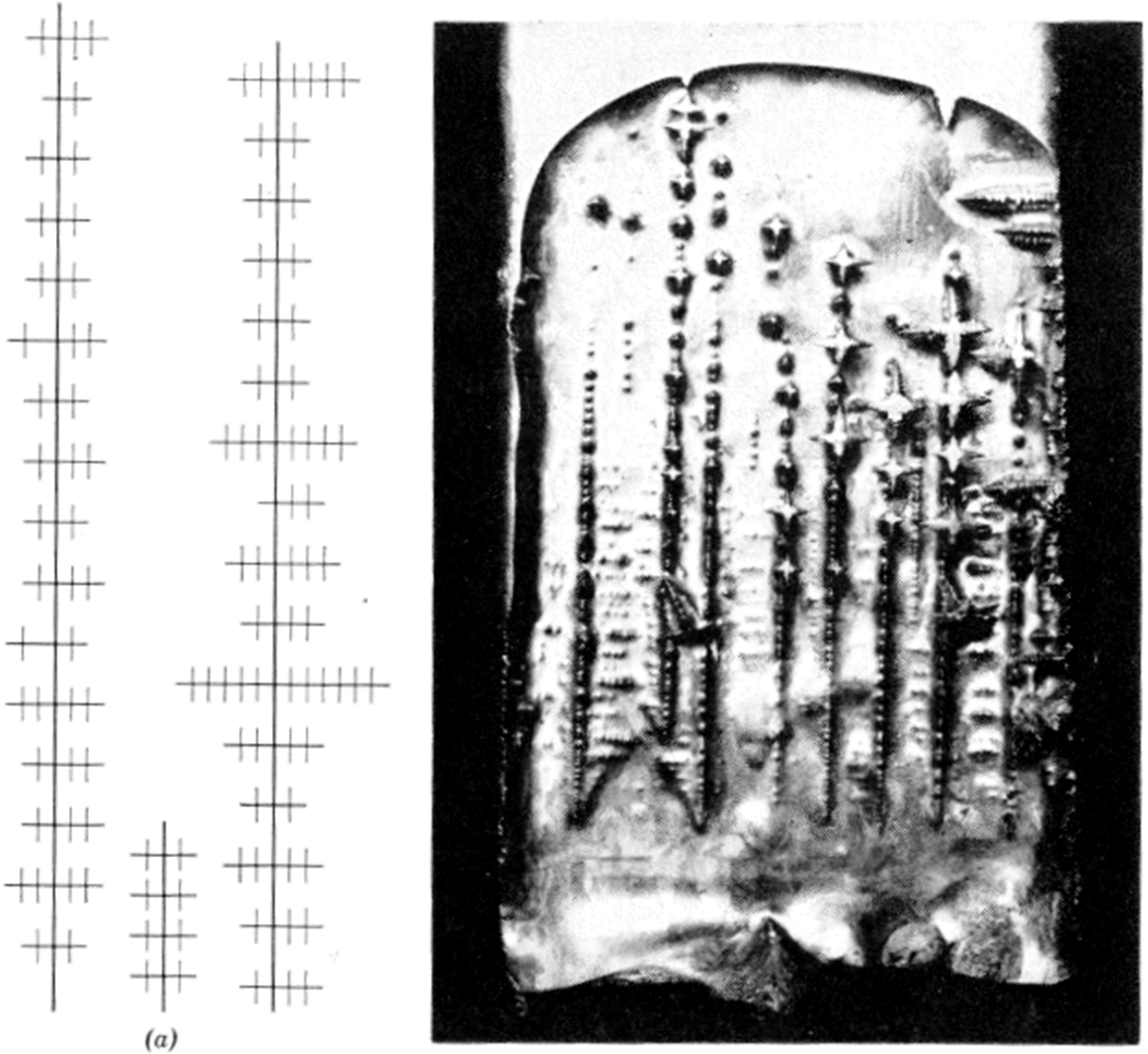
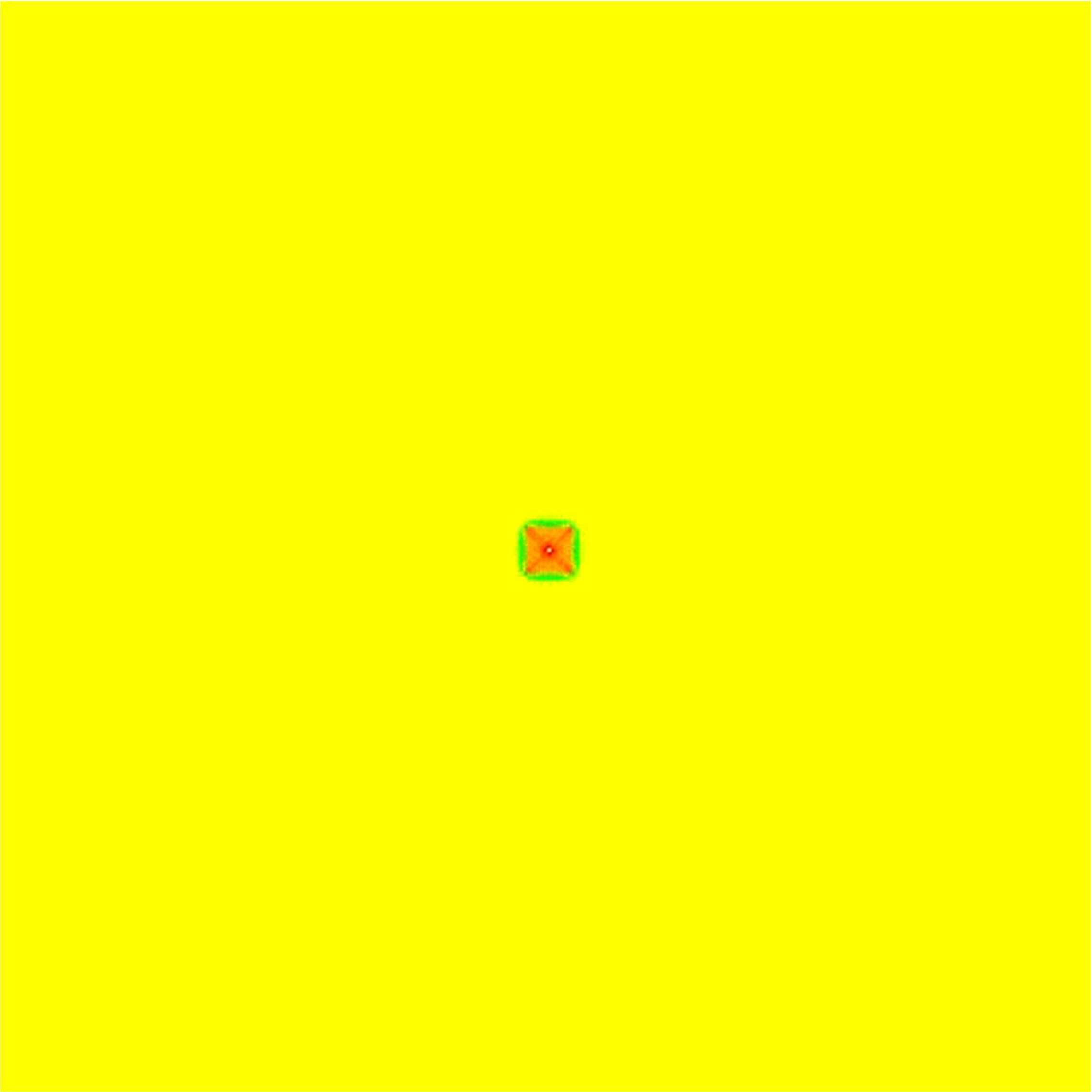


Fig. 4.3. Lead dendrites. (*a*) Schematic, (*b*) photograph. Photograph by F. Weinberg.

Solidification: Liquid ⟶ Solid



4 Fold Symmetric Dendrite Array

Effect of surfaces and of grain boundaries.

Grain boundary lies in the solid in a plane perpendicular to the solid-liquid interface.

→ They assume that thermodynamic equilibrium is maintained at all times.

→ A groove should exist at the boundary, a result that can be derived from the static equilibrium of the intersection of two surfaces.

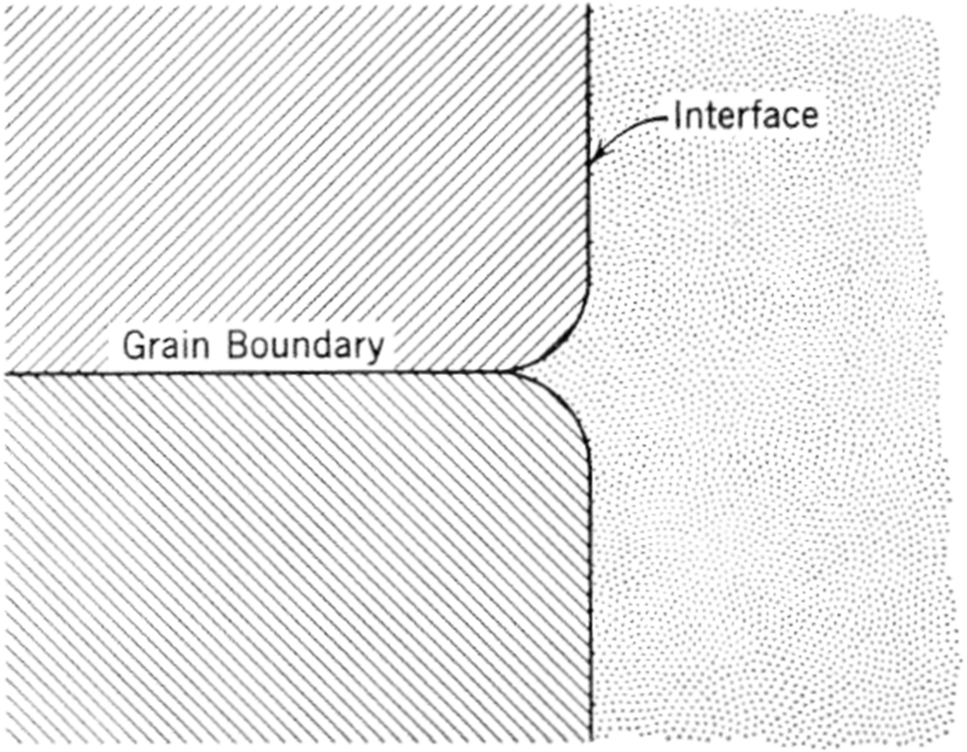


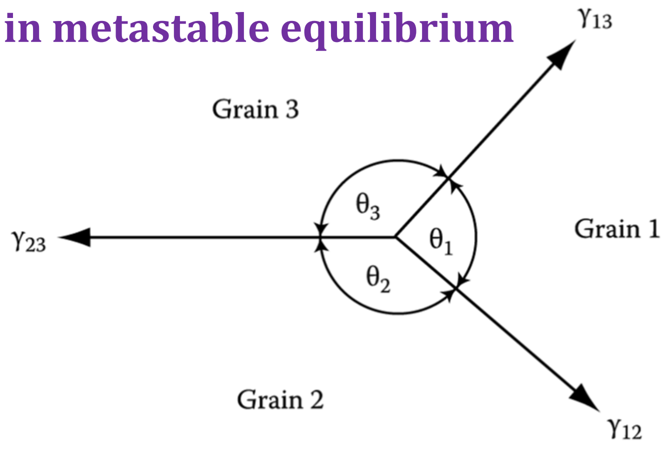
Fig. 4.7. Effect of grain boundary on interface shape.

If the boundary E is independent of orientation,

* General high angle boundary : $d\gamma/d\theta \approx 0$ (GB behaves like a soap film)

→ Under these conditions the requirements for metastable equilibrium at junction between three grains is that the boundary tensions $\gamma_{13}, \gamma_{23}, \gamma_{12}$ must balance.

The balance of GB tensions for a GB intersection in metastable equilibrium



$$\boxed{\frac{\gamma_{23}}{\sin\theta_1} = \frac{\gamma_{31}}{\sin\theta_2} = \frac{\gamma_{12}}{\sin\theta_3}} \quad \text{(Eq. 3.13)}$$

if all GBs have same GB energy independent of boundary orientation

→ **θ = 120°**

Eq. 3.13 applies to any three boundaries i.e. grain 1~ different phase to grain 2 & 3.

Ex) If the solid-vapor energy ($\gamma_{S/V}$) is the same for both grains,

$$2\gamma_{SV}\cos\frac{\theta}{2} = \gamma_b$$

(Here, presence of any torque terms ~ neglected)

One method of measuring GB energy:

: anneal a specimen at a high temp. and then measure the angle at the intersection of the surface with B.

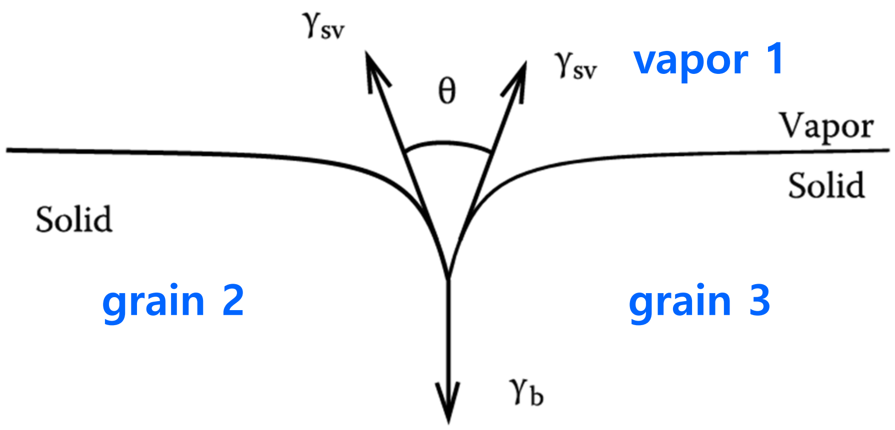


Fig. 3. 18 The balance of surface and grain boundary tensions at the intersection of a grain boundary with a free surface.

Effect of surfaces and of grain boundaries.

Grain boundary lies in the solid in a plane perpendicular to the solid-liquid interface.

→ They assume that thermodynamic equilibrium is maintained at all times.

→ A groove should exist at the boundary, a result that can be derived from the static equilibrium of the intersection of two surfaces.

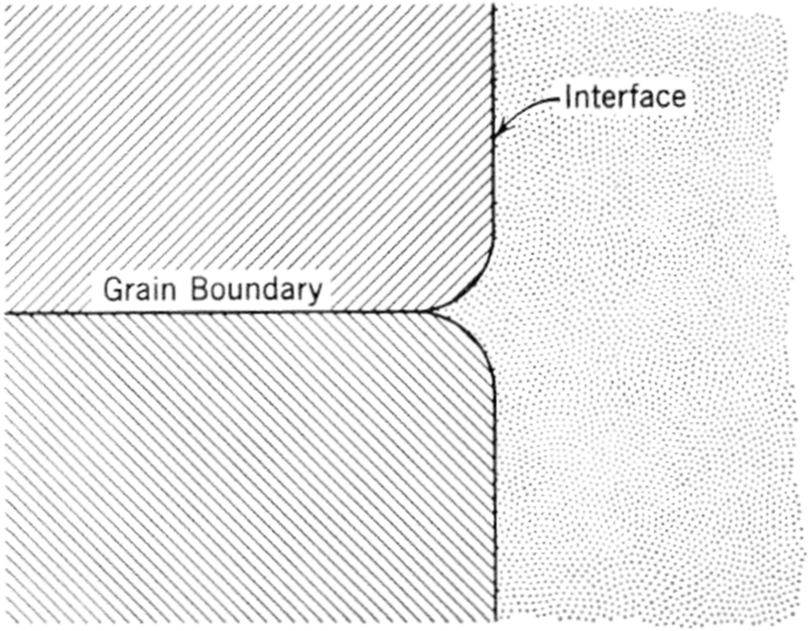


Fig. 4.7. Effect of grain boundary on interface shape.

⇨ **The groove may be asymmetric if the surface free energies are not equal and that this can lead to the formation of grain boundaries in directions that are not normal to the solid-liquid interface. → "development of preferred orientations" (Chapter 8)**

Dendritic solidification

1) Occurrence of branching can be looked upon in much same way.

(a) A primary arm is itself in a region of temperature inversion.

(b) Uniform radial growth of the cylindrical primary arm would be unstable.

(c) A series of branches would occur, spaced at intervals determined by the latent heat evolved from the branches themselves.

(d) The same process can repeat on a finer and finer scale until there is not sufficient supercooling to develop the irregularities of growth into branches.

2) Rate of growth at any given point is controlled by the rate of heat loss at that point.

(a) Substances that grow with a "smooth interface" can grow only by the lateral extension of existing steps, unless the supercooling is very large.

→ at moderate supercooling ~ growth by perpetual steps provided supercooling

→ the face will be nearly flat, since each step travels outward to the limit set by the layer below; all points on the same face must grow at the same speed.

→ The faces will be slightly convex. (Fig. 4.9)

Dendritic solidification

Each face on which growth takes place requires at least one dislocation.

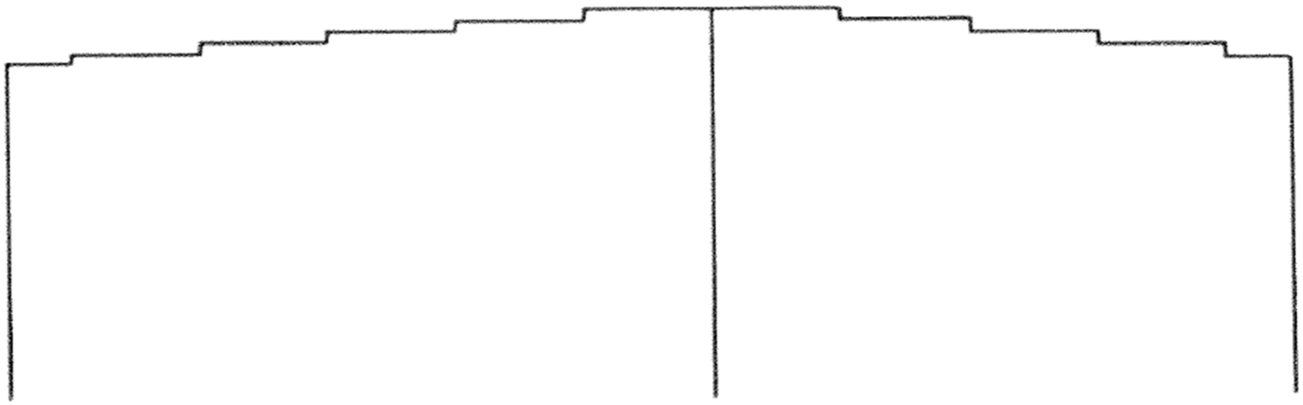


Fig. 4.9. Shape of surface resulting from growth by dislocation mechanism.

(b) A crystal face that has a "diffuse interface" can grow at different rates at different points on the same face, which would be required if growth were controlled by the local heat flow.

→ Growth ~ greater near the corners and the edges than at the centers of faces.

→ Dendritic growth is restricted to substances and growth conditions in which the solid-liquid interfaces are not completely smooth.

a) "Ribbon" crystals

* Crystals of silicon, germanium, and bismuth with a "smooth interface"

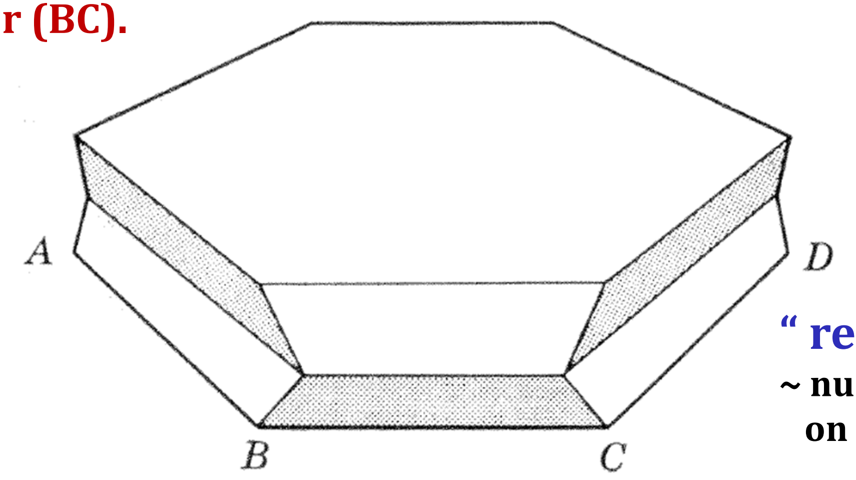
under ordinary growth conditions

→ Crystals are grown by "pulling" at a controlled speed from a supercooled melt.

→ a thin "ribbon-shaped" crystal, with its two flat {111} surfaces parallel to a closely packed plane & growth directions <112>_diamond cube structure

→ Sometimes some branching at the edge of the ribbons ~ always within the space bounded by the two planes which define the surfaces of the ribbon

If a twinned crystal is bounded only by {111} plane, it will be of hexagonal shape and the twin plane will "crop out" as an "edge" which alternates between re-entrant (AB and CD) and exterior (BC).



" re-entrant twin edge "

~ nucleation site for new layers on the edges of the sheet

Fig. 4.10. Geometry of "ribbon" crystal.

b) "Feather" growth_in "diffuse interface" when ΔT at interface is so small

: appear to resemble "ribbon" crystals ~ always contain twin planes
(But it is not obvious why a twin mechanism should come into play in a material)

→ Grow only when the supercooling at the interface is so small that the diffuseness of the interface is insufficient to allow new layers to form.

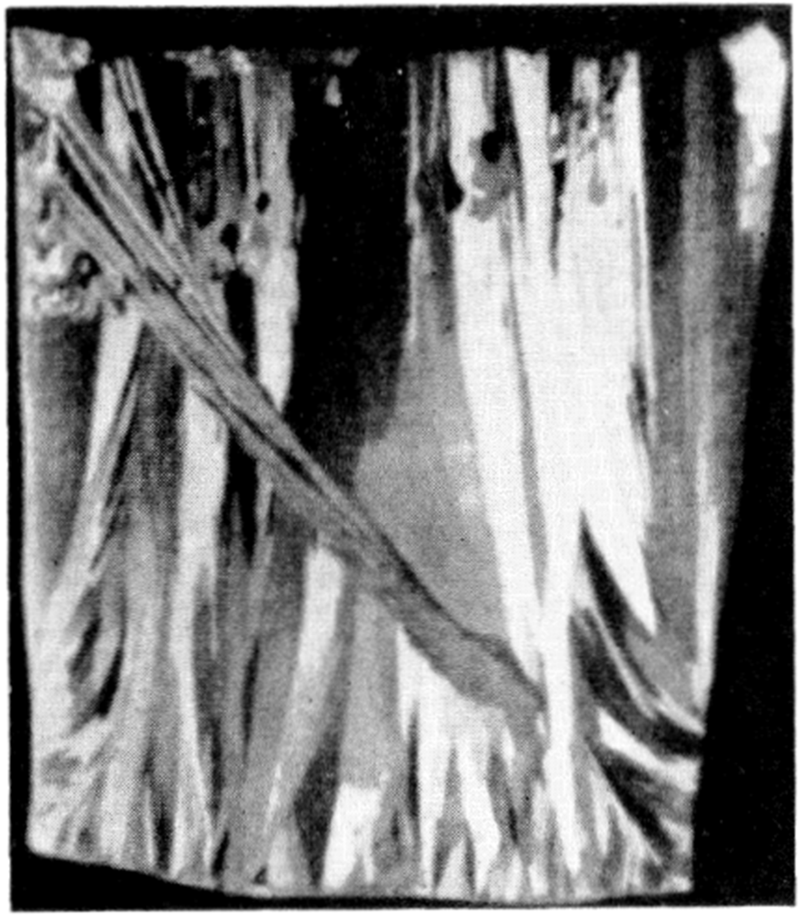


Fig. 4.11. "Feather" crystals. [From Brenner and Roth, *Z. Metallkunde*, **32**, 10 (1940).]

c) “flat dendrites”

: ICE, where growth takes place dendritically in basal plane of the structure and much more slowly, and with a flat interface, in perpendicular direction.

→ The difference between the growth habits in and normal to the basal plane is attributed to the existence of a smooth interface parallel to the basal plane and a diffuse interface at all other orientation.

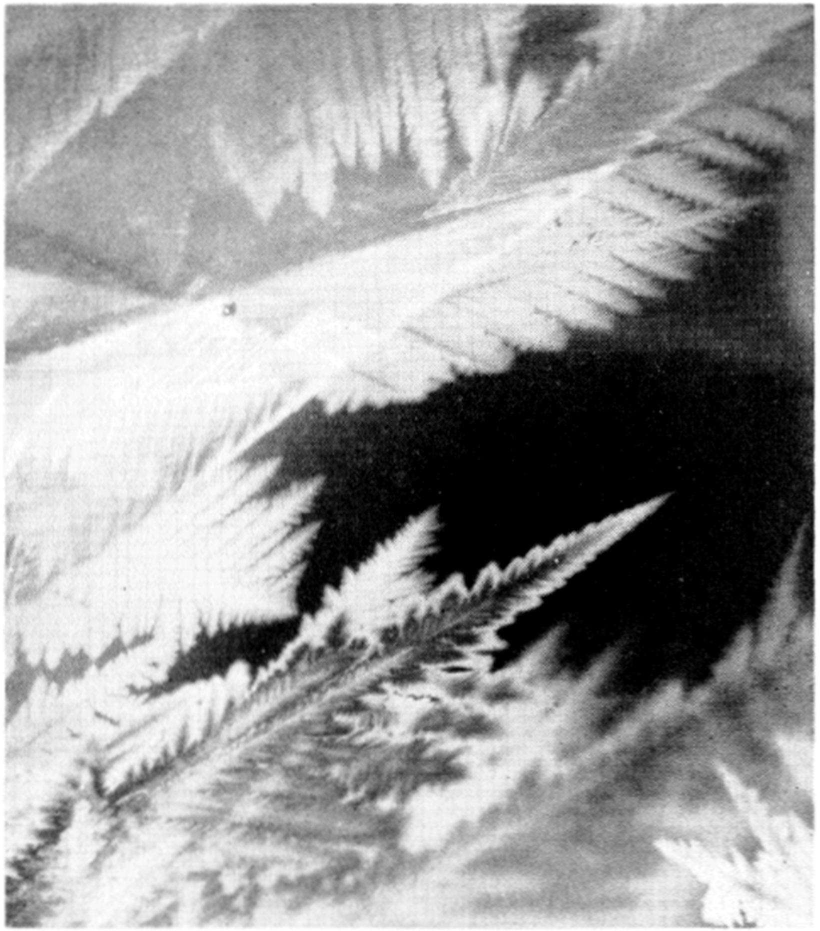


Fig. 4.12. Dendritic morphology of ice growing in water at −1.5°C. Photograph by R. B. Williamson.

4.5 Dendritic Growth

For aspects of dendritic growth

(a) Total amount of solid formed as a function of initial supercooling of the liquid

(b) Speed of growth as a function of the temperature of the liquid

(c) Direction of growth in relation to the structure of the growing crystal

(d) Spacing and relative lengths of the branches

(1) Total amount solidified. **Assumption: liquid is cooled to a uniform temperature (below T_E), isolated so that no heat may enter or leave it. → "Total amount of Dendritic growth"**

L be the latent heat
C_S and C_L the specific heat of solid and liquid, and
ΔT the initial supercooling

then the fraction solidifying, S, is given by the equation

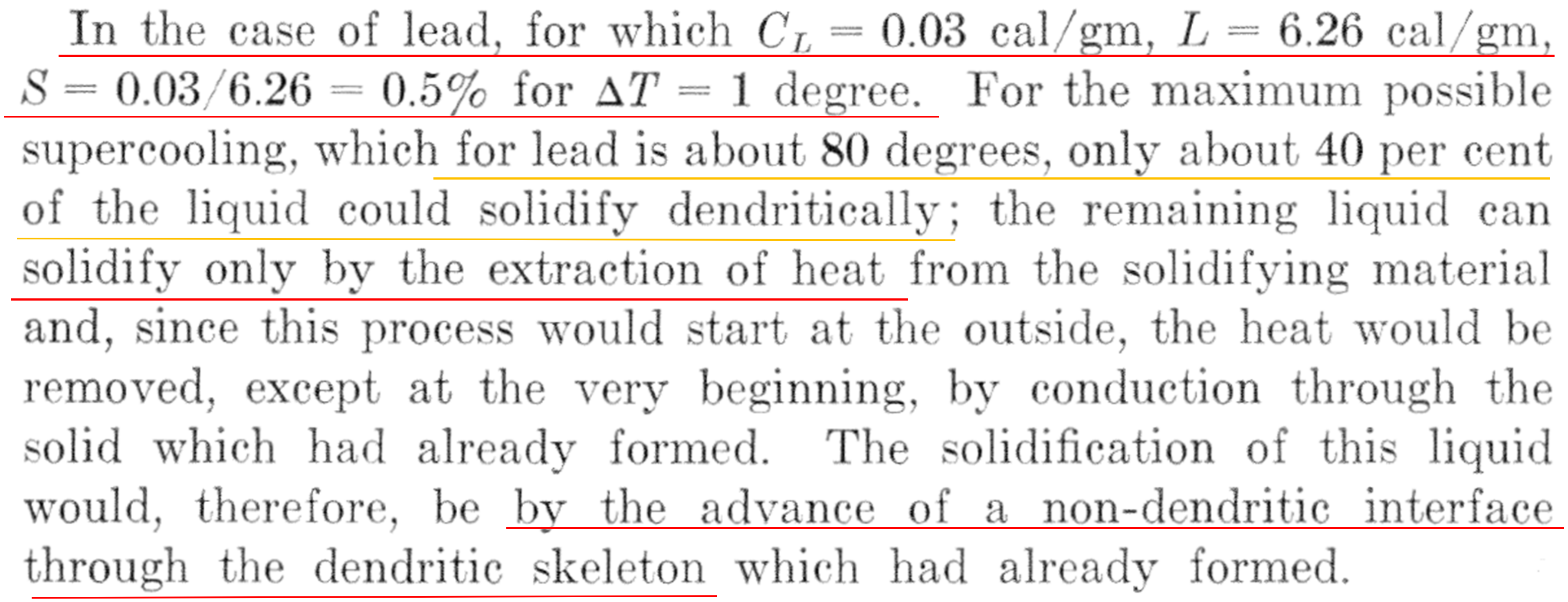
$$SL = C_L\left(1 - \frac{S}{2}\right)\Delta T + C_S\frac{S}{2}\Delta T$$

assuming that L, C_L, and C_S are independent of temperature; hence

$$\boxed{S = \frac{2C_L\Delta T}{2L - (C_L - C_S)\Delta T}}$$

or, if the two specific heats are assumed to be equal, and if ΔT is small, then $\boxed{S \approx C\Delta T/L.}$ **(C_L=C_S)**

$$\boxed{S = \frac{2C_L \Delta T}{2L - (C_L - C_S)\Delta T}} \Rightarrow \boxed{S \approx C\Delta T/L.}$$



In the case of lead, for which $C_L = 0.03$ cal/gm, $L = 6.26$ cal/gm, $S = 0.03/6.26 = 0.5\%$ for $\Delta T = 1$ degree. For the maximum possible supercooling, which for lead is about 80 degrees, only about 40 per cent of the liquid could solidify dendritically; the remaining liquid can solidify only by the extraction of heat from the solidifying material and, since this process would start at the outside, the heat would be removed, except at the very beginning, by conduction through the solid which had already formed. The solidification of this liquid would, therefore, be by the advance of a non-dendritic interface through the dendritic skeleton which had already formed.

→ "Filing in" stage (much slower than the dendritic growth)

Q: How to calculate the growth rate (v) in the tip of a growing dendrite?

Closer look at the tip of a growing dendrite

different from a planar interface because heat can be conducted away from the tip in three dimensions.

Assume the solid is isothermal $\left(T_S' = 0\right)$

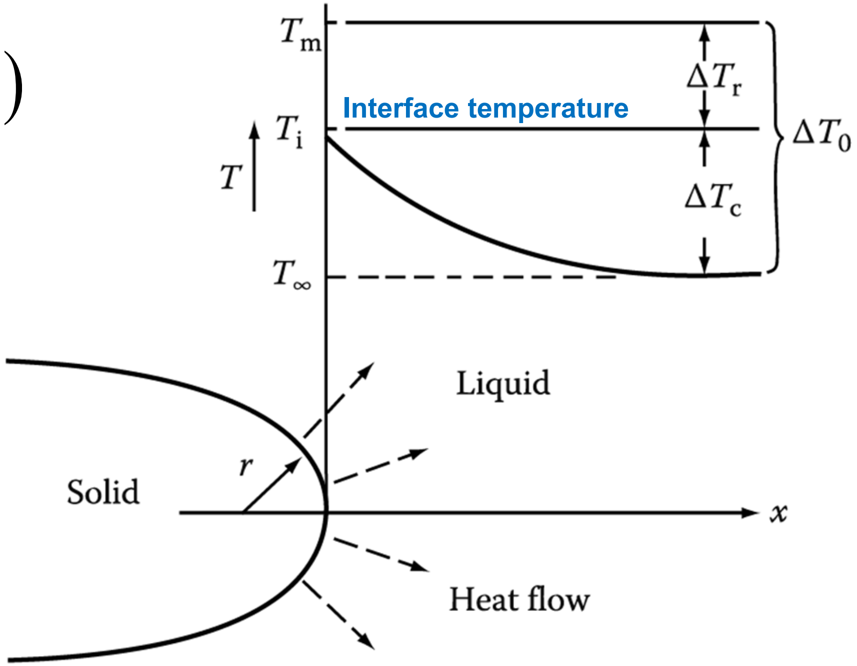
From $K_S T_S' = K_L T_L' + v L_V$

$$If\ \ T_S' = 0,\ \ v = \frac{-K_L T_L'}{L_V}$$

A solution to the heat-flow equation for a hemispherical tip:

$$T_L'(negative) \cong \frac{\Delta T_C}{r} \qquad \Delta T_C = T_i - T_\infty$$

$$v = \frac{-K_L T_L'}{L_V} \cong \frac{K_L}{L_V} \cdot \frac{\Delta T_C}{r} \qquad v \propto \frac{1}{r}$$



However, ΔT_r also depends on r. How?

Thermodynamics at the tip?

Gibbs-Thomson effect:
melting point depression

$$\Delta G = \frac{L_V}{T_m}\Delta T_r = \frac{2\gamma}{r} \qquad \boxed{\Delta T_r = \frac{2\gamma T_m}{L_V r}}$$

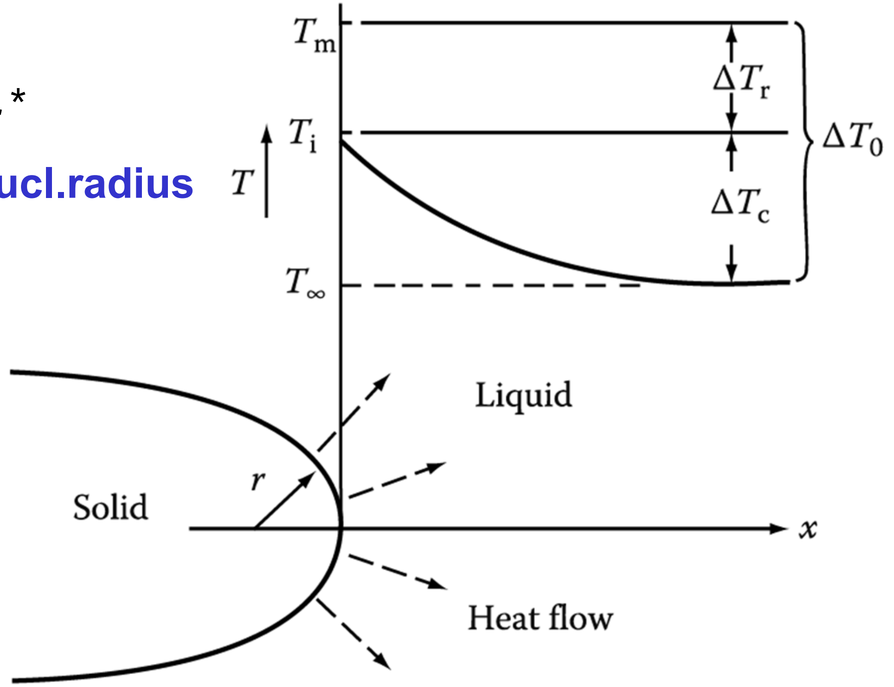
Minimum possible radius (r)?

$$r_{min} : \Delta T_r \rightarrow \Delta T_0 = T_m - T_\infty \rightarrow r^*$$

The crit.nucl.radius

$$\boxed{r^* = \frac{2\gamma T_m}{L_V \Delta T_o}}$$

$$\Delta T_r = \frac{2\gamma T_m}{L_V r}$$



Express ΔT_r by r, r^* and ΔT_o.

$$\Delta T_r = \frac{r^*}{r} \Delta T_o$$

$$\boxed{v \cong \frac{K_L}{L_V} \cdot \frac{\Delta T_c}{r} = \frac{K_L}{L_V} \cdot \frac{(\Delta T_0 - \Delta T_r)}{r} = \frac{K_L}{L_V} \cdot \frac{\Delta T_0}{r}\left(1 - \frac{r^*}{r}\right)}$$

$v \rightarrow 0$ *as* $r \rightarrow r^*$ *due to Gibbs-Thomson effect* $\Delta T_r \rightarrow \Delta T_0$

$v \rightarrow 0$ *as* $r \rightarrow \infty$ *due to slower heat condution*

Maximum velocity?

$$\boxed{\rightarrow \; r = 2r^*}$$

(2) Speed of growth

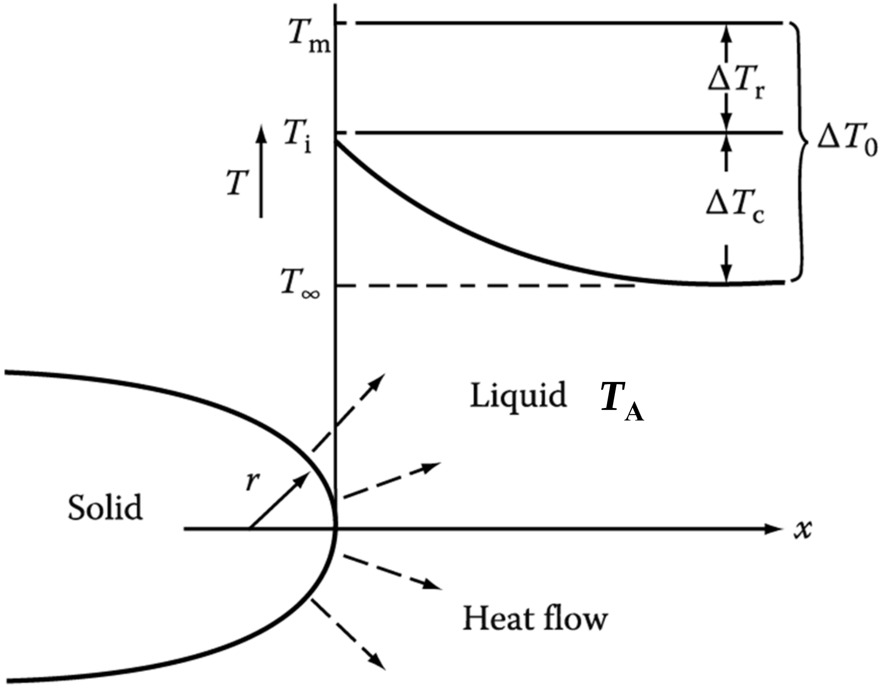
: depends on the shape and size of the tip and on its temperature

(a) Steady state theories

Assumption of Fisher : a) tip ~ spherical and isotropic

b) kinetic driving force ~ 0 (ΔT between interface and equilibrium)

c) spherical tip loses heat by radial conduction & moves forward with its shape unchanged



Rate of loss of heat H from the Hemi-sphere at steady state

$$H = 2\pi r K (T_i - T_A)$$

Rate of advance of the tip (V) : volume solidified per unit time divided by the area of cross section

$$v = \frac{H}{L\rho\pi r^2}$$

$$v = \frac{2K}{L\rho r}(T_I - T_A)$$

i.e., it must be the critical radius for the actual interface temperature; therefore,

$$r^* = \frac{2\sigma T_E}{L\Delta T} \longrightarrow r = \frac{2\sigma T_E}{L(T_E - T_I)} \longrightarrow v = \frac{2K}{L\rho r}(T_I - T_A)$$

Using this expression for r, the value of v is given by

$$\begin{aligned} v &= \frac{2KL(T_E - T_I)}{2L\rho\sigma T_E}(T_I - T_A) \\ &= \frac{K}{\rho\sigma T_E}(T_E - T_I)(T_I - T_A) \end{aligned}$$

which cannot be solved for v without further assumptions because T_I is unknown.

Maximum value of *v* :

When $(T_E - T_i) = (T_i - T_A)$ $\longrightarrow$ $v = K(\Delta T)^2/4\rho\sigma T_E$ **(here, $\Delta T = T_E - T_A$)**

$$v \propto (\Delta T)^2$$

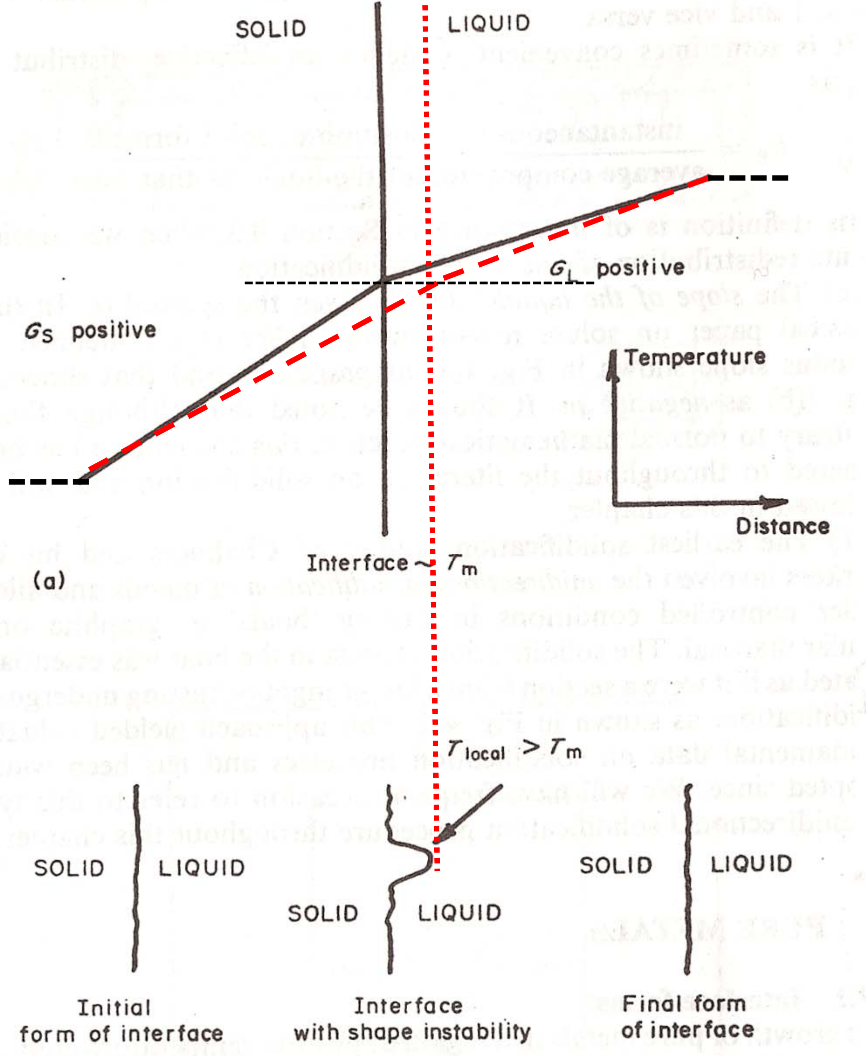
However, the quantitative agreement is poor; for example, for tin (Sn), ***v*** should be about **7**$(\Delta T)^2$, but experimentally it is about $v \propto$ **0.1**$(\Delta T)^2$

Chapter 4. Microscopic Heat Flow Considerations

"Removal of latent heat" → Heat Flow and Interface Stability

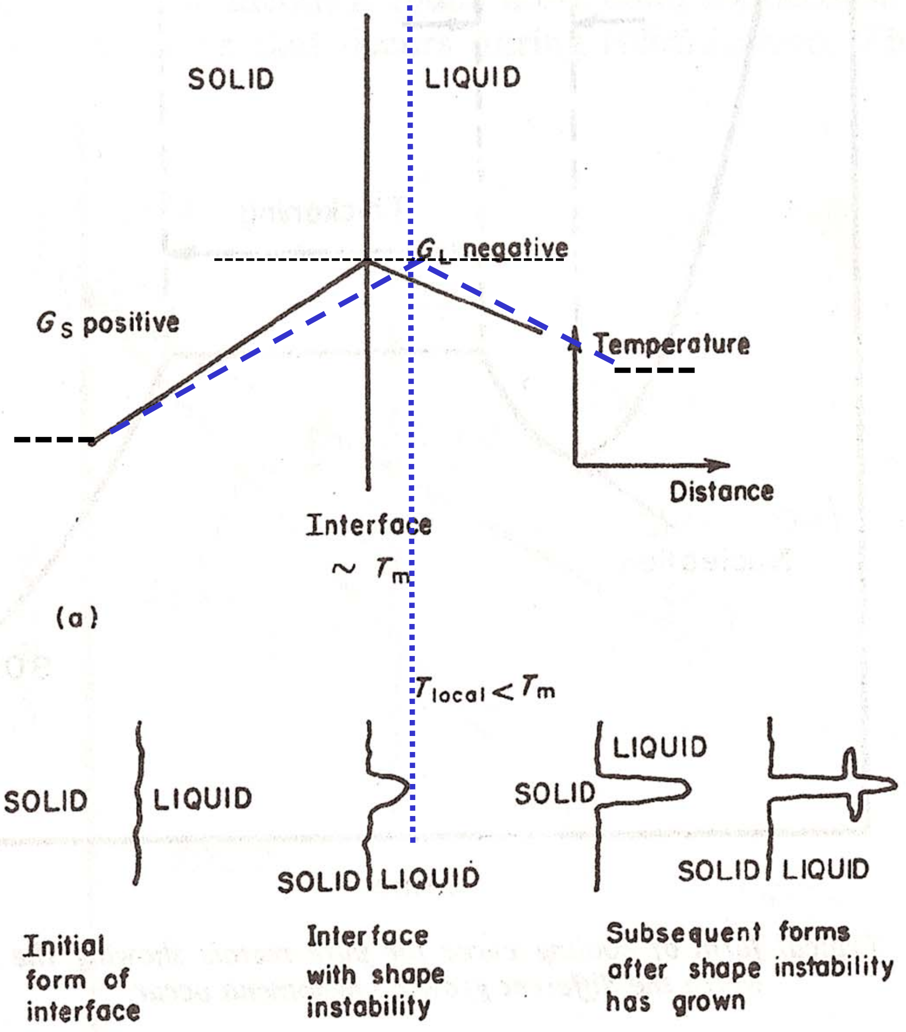
1) Superheated liquid

: Extraction of latent heat by conduction in the crystal



2) Supercooled liquid

: conduction of latent heat into the liquid

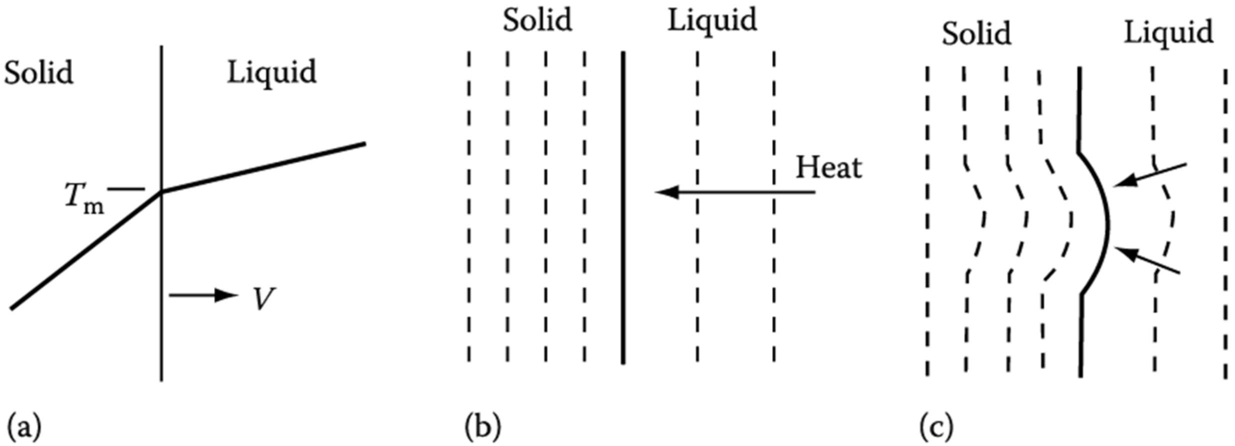


Heat Flow and Interface Stability - Planar interface

1) Superheated liquid: Extraction of Latent Heat by Conduction into the Crystal

Consider the solidification front with heat flow from L to S.

solid growing at v
(planar)



Heat flow away from the interface through the solid $K_S T'$

$K_L T'_L$ **- Heat flow from the liquid**

vL_V **- Latent heat generated at the interface**

Heat Balance Equation

$$K_S T'_S = K_L T'_L + vL_V$$

K: thermal conductivity

If r is so large → Gibbs-Thompson effect can be ignored the solid/liquid interface remain at T_m
(r : radius of curvature of the protrusion / $K_S > K_L$)

dT/dx in the liquid ahead of the protrusion will increase more positively. $T_L'\uparrow$ & $T_S'\downarrow$

More heat to the protrusion → melt away

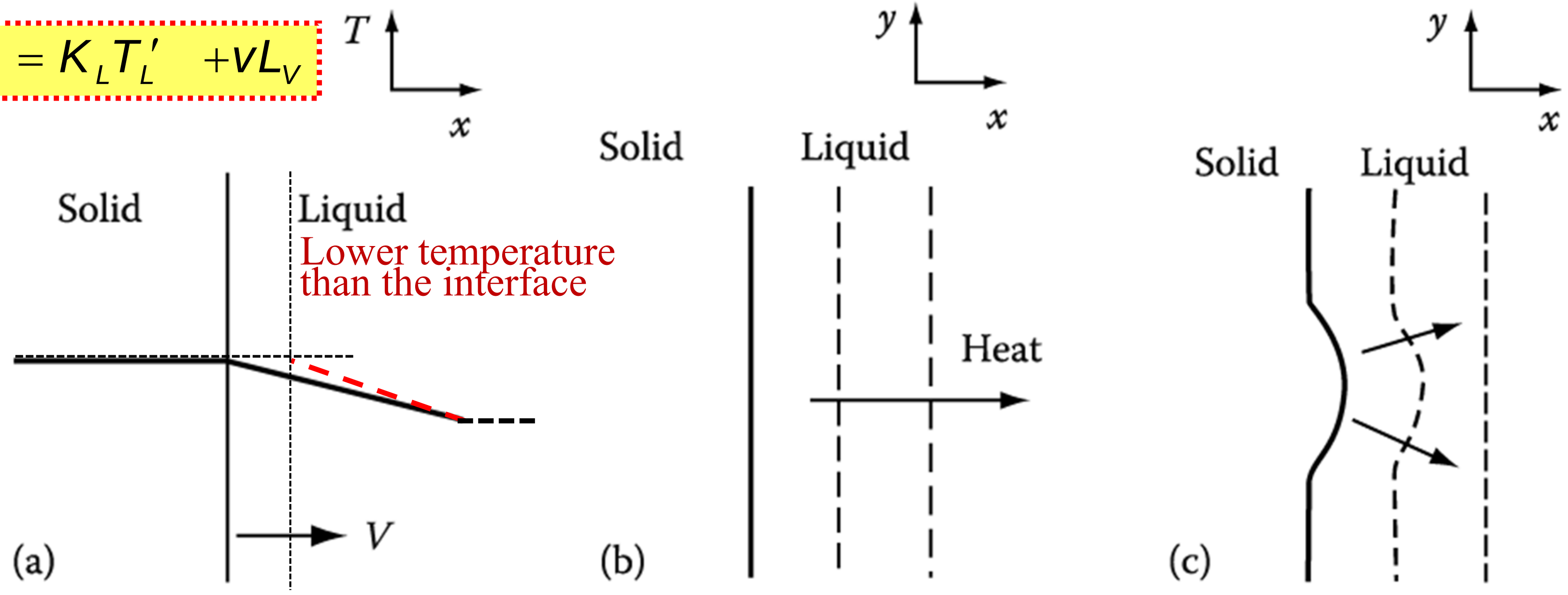
v of protrusion ↓ to match other v in planar region

mould walls

Heat Flow and Interface Stability - **Planar interface**

2) Solid growing into SCL: conduction of latent heat into the liquid

$$K_S T'_S = K_L T'_L \quad + vL_V$$



(a) Dendritic growth take place when, and only when, the melt is supercooled.

(b) Growth would be relatively slower near the plane, because the supercooling would be less there.

(c) The directions of growth are always strictly crystallographic.

(d) Branching occurs at roughly regular spacing, smaller for each successive order of branching.

- protrusion $\dfrac{dT_L'}{dX} < 0$ **becomes more negative**

→ heat flow from solid = the protrusion grows preferentially.

Effect of grain boundaries on S/L interface stability

Grain boundary lies in the solid in a plane perpendicular to the solid-liquid interface.

→ They assume that thermodynamic equilibrium is maintained at all times.

→ "A groove" should exist at the boundary, a result that can be derived from the static equilibrium of the intersection of two surfaces.

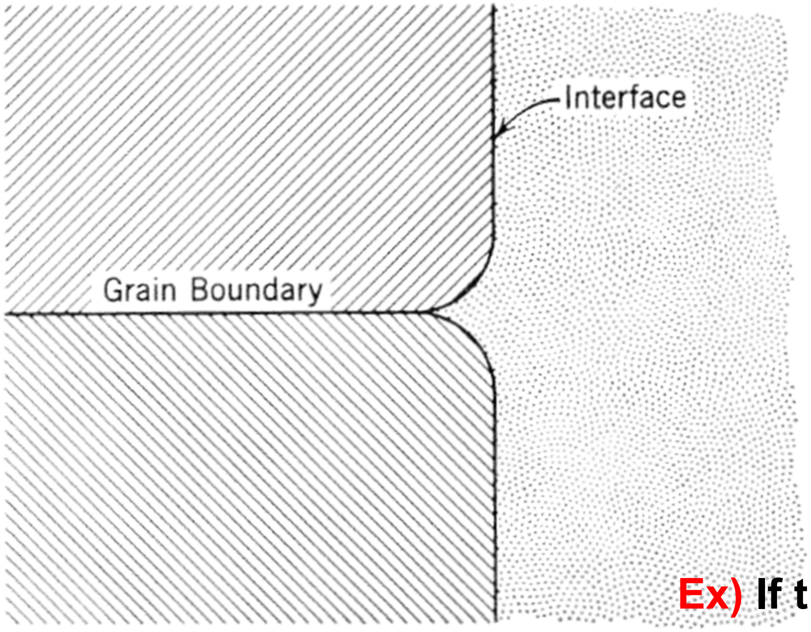
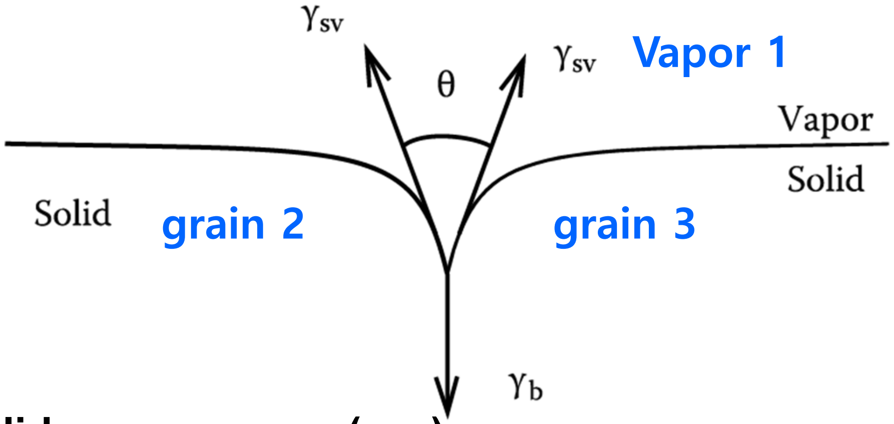


Fig. 4.7. Effect of grain boundary on interface shape.

One method of measuring GB energy:

: anneal a specimen at a high temp. and then measure the angle at the intersection of the surface with B.



Ex) If the solid-vapor energy ($\gamma_{S/V}$) is the same for both grains,

$$2\gamma_{SV}\cos\frac{\;}{2}=\gamma_b$$

(Here, presence of any torque terms ~ neglected)

⇨ The groove may be asymmetric if the surface free energies are not equal and that this can lead to the formation of grain boundaries in directions that are not normal to the solid-liquid interface. → "development of preferred orientations" (Chapter 8)

Characteristics of Dendritic Solidification

1) Occurrence of branching can be looked upon in much same way.

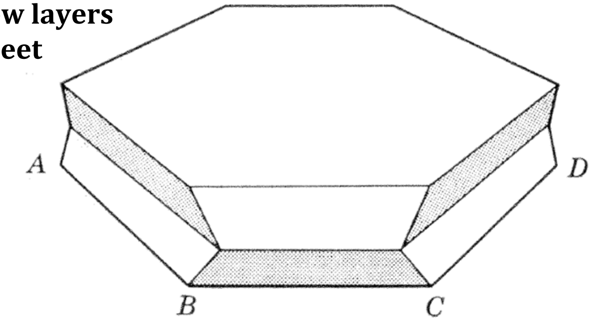
2) Rate of growth at any given point is controlled by the rate of heat loss at that point.

(a) Substances that grow with a smooth interface can grow only by the lateral extension of existing steps, unless the supercooling is very large.

(b) A crystal face that has a diffuse interface can grow at different rates at different points on the same face, which would be required if growth were controlled by the local heat flow.

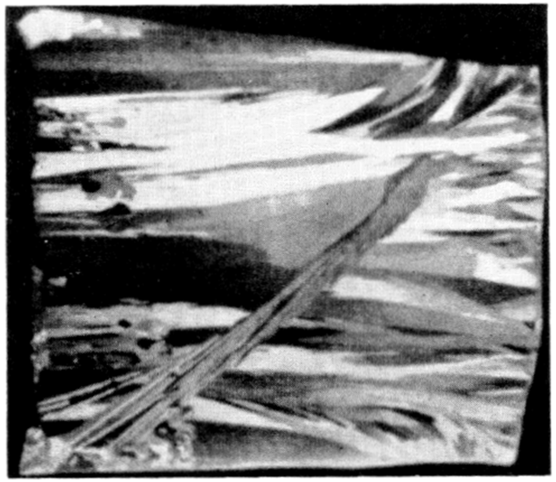
→ Dendritic growth is restricted to substances and growth conditions in which the solid-liquid interfaces are not completely smooth.

c) “Ribbon” crystals



“ re-entrant twin edge “
~ nucleation site for new layers
on the edges of the sheet

* Crystals of silicon, germanium, and bismuth
with a smooth interface under ordinary growth conditions
→ lateral growth/ orientation

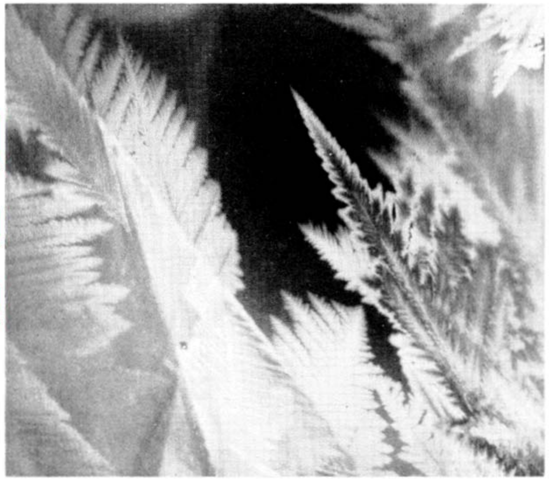


b) “Feather” growth

* in “diffuse interface” when ΔT at interface is so small

→ Grow only when the supercooling at the interface
is so small that the diffuseness of the interface is
insufficient to allow new layers to form

c) “flat dendrites”



: ICE, where growth takes place dendritical
plane of the structure and much more slow
with a flat interface, in perpendicular dire

→ the existence of a smooth interface parallel
to the basal plane and a diffuse interface
at all other orientation.

4.5 Dendritic Growth

For aspects of dendritic growth

(a) Total amount of solid formed as a function of initial supercooling of the liquid

(b) Speed of growth as a function of the temperature of the liquid

(c) Direction of growth in relation to the structure of the growing crystal

(d) Spacing and relative lengths of the branches

(1) Total amount solidified. **Assumption: liquid is cooled to a uniform temperature (below T_E), isolated so that no heat may enter or leave it. → "Total amount of Dendritic growth"**

$$\boxed{S = \frac{2C_L\Delta T}{2L - (C_L - C_S)\Delta T}} \Rightarrow \boxed{S \approx C\Delta T/L.}$$

Others → "Filing in" stage

(much slower than the dendritic growth)

(2) Speed of growth

: depends on the shape and size of the tip and on its temperature

a) Steady state theory

Maximum value of v :

When $(T_E - T_i) = (T_i - T_A)$ $\longrightarrow$ $v = K(\Delta T)^2/4\rho\sigma T_E$ **(here, $\Delta T = T_E - T_A$)**

$$v \propto (\Delta T)^2$$

* Modification of examination of Fisher's analysis:

(a) To select a shape that can propagate without change

(b) To recognize that the surface may not be isothermal

(c) To introduce a term for the kinetic driving force

(d) To include the possibility that the kinetic rate constant depends on surface orientation

1) Chalmers and Jackson

Departure from the $v \propto (\Delta T)^2$ law : a) kinetic term ~ unresonably large

b) hemi-sphere could not move forward without increase of radius.

⟶ More "pointed" shape would improve the quantitative agreement

2) Horvay and Cahn

Elliptical paraboloid with isothermal surface would advance under steady sate conditions (i.e. at a constant velocity & constant shape). (r=tip radius)

$v \propto (\Delta T)^n / r$

Previously, n→ 1

➡ n→1.2 for a paraboloidal dendritic of circular section to

n→ 2 for a dendritic platelet

* However, Horvay and Cahn reiterate that conclusion referred to above,

(a) heat transfer equation along close not provide sufficient information to lead to a prediction of the actual velocity as a function of ΔT.

(b) Assumption of uniform surface temperature ~ not realistic

However, this would require only a small correction.

3) Bolling and Tiller

Reflect non-uniformity of surface temp. → stable shape change slightly from a paraboloid

B&T follow the physical basis proposed by Fisher $\longrightarrow$ $v_{max} \propto (\Delta T)$

(b) Non-steady state theory

True steady state conditions can be achieved in the growth of a silicon ribbon crystal and the relationship btw the various parameter can be analyzed realistically in terms of heat flow from the advancing "tip" or "edge". However, the periodic occurrence of branching in dendrites of metals or ice suggests that the size of the tip and the temperature distribution around it may fluctuate in a periodic manner. (non-steady state condition)

Tip should grow until it becomes large enough to be unstable and then break down into a number of separate tips, each of smaller radius. → Each of these tips again grow until it becomes unstable.

Growth vs. branching of dendrite: periodicity of process

→ overall control: by heat flow into a colder liquid ~ unchanged

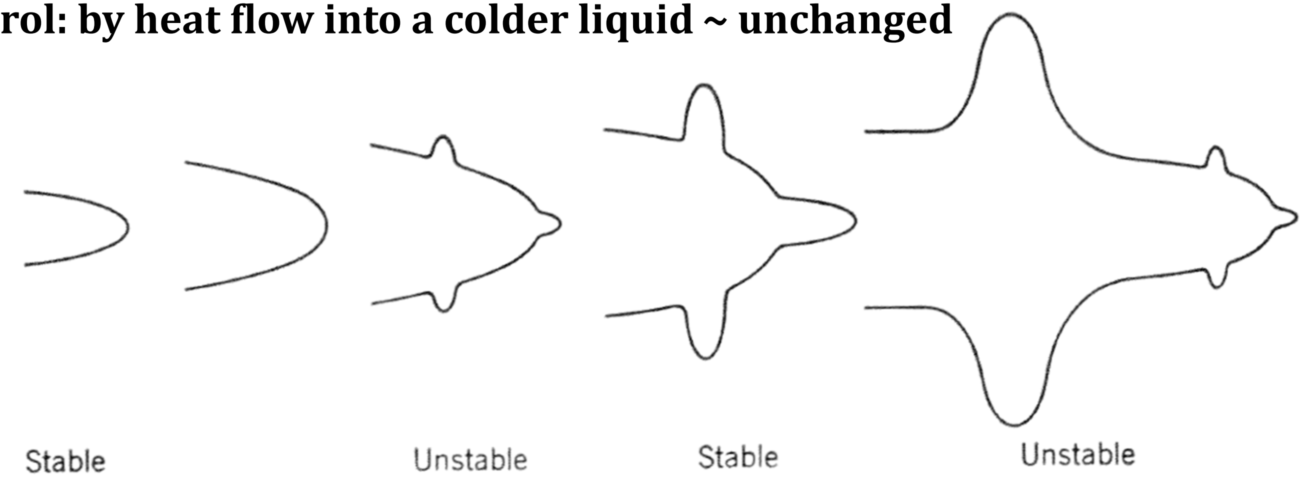


Fig. 4.14. Branching of dendrites.

Theories are developed for a single isolated dendritic spikes. But real growth and branching of dendrite are influenced by the thermal field of its neighbors.

* $\overline{PB} < \overline{PA}$ → $v_{\overline{PB}} = v_{\overline{PA}}$ → regular hexagon without re-entrant angles : Fig. 4.15. (c)

Secondary arm Primary arm

- Only difference between primary spike ($\overline{PA}$) and the secondary spike ($\overline{PB}$):
$\overline{PB}$ exhibit parallel array which is retarded by the thermal field of its neighbors.
- Speed ratio of free spike ($\overline{PA}$)와 retarded spike ($\overline{PB}$)– PAB 60° angle
→ This angle is less than 60° only at small undercooling, showing that the mutual interference of neighboring spikes is important only when growth is slow.

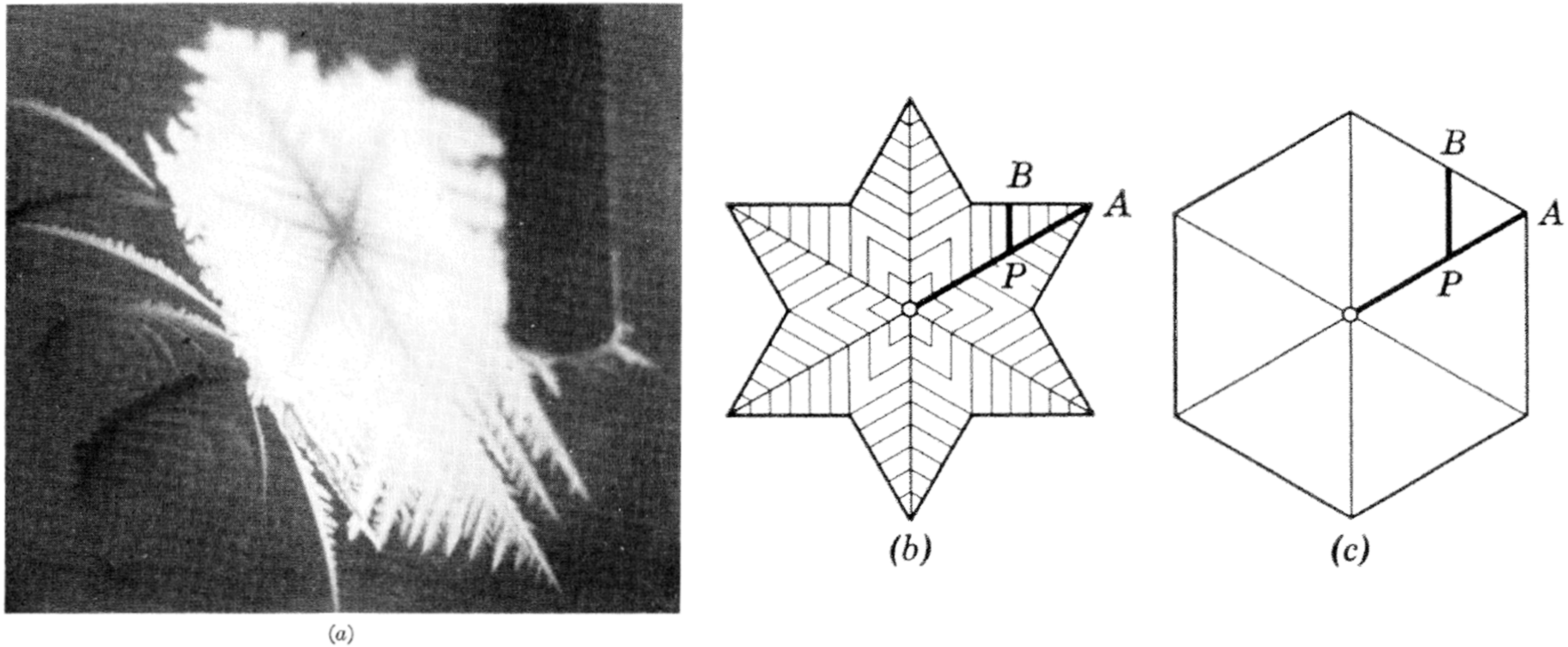


Fig. 4.15. Morphology of ice dendrites; (a) photograph of a dendrite, (b) schematic, (c) ideal

* Growth velocity of dendrite

A member of a row < a spike isolated dendrite

- Each dendrite of a 2D array will grow even more slowly as a result of their mutual interferernce by the overlapping of their thermal fields.

* EXPERIMENTAL OBSERVATION OF RATE OF DENDRITIC GROWTH

- Growth of crystals in contact with a solid substrate bear little relationship to the results obtained in free growth in the liquid.

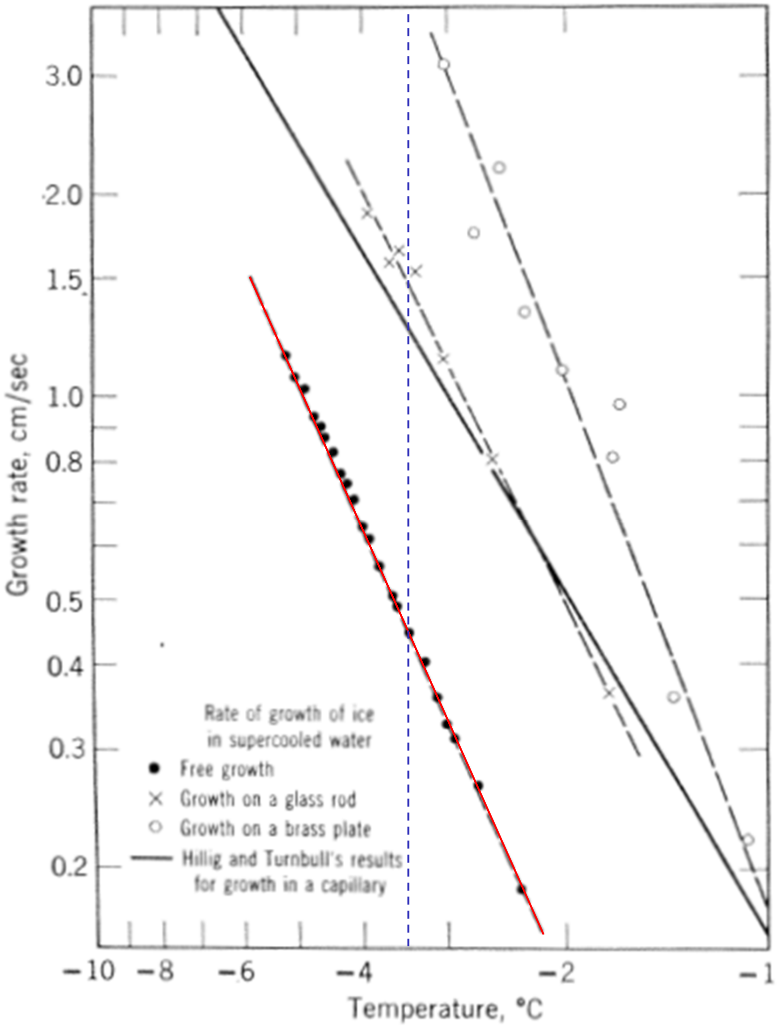


Fig. 4.16. Effect of substrate on rate of growth of ice in supercooled water

Growth in solid substrate at the same ΔT
Faster than free growth case

* Experimental observation on rates of freely growing dendrite

a) Weinberg and Chalmers:

lead dendrite grew much faster than the smooth interface

b) Rosenberg and Winegard:

R (growth rate) data: Scattering

Why?

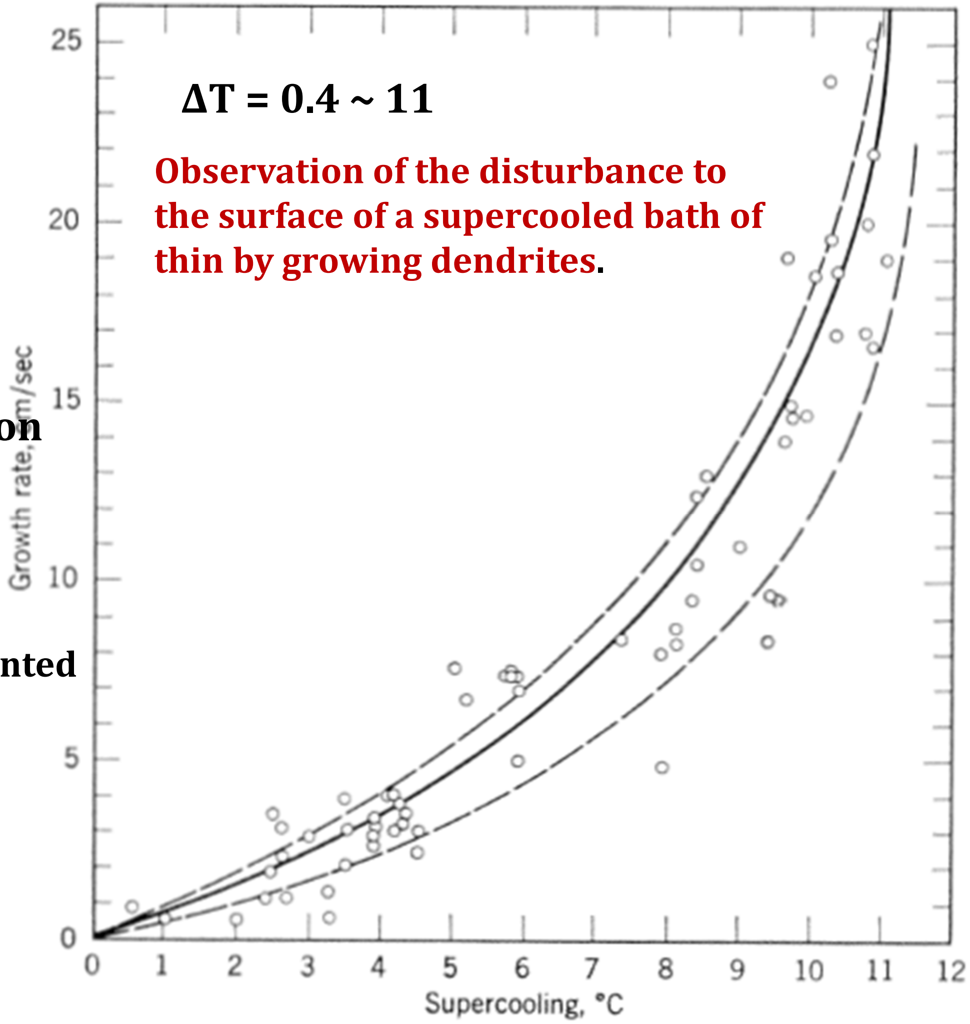
Dendrites, which were nucleated by local cooling of the melt, grew with random orientations

∵ Dendrite in Pb always grow in cube direction

→ Distance traveled by a dendrite while advancing one unit of distance in the <111> direction would be $\sqrt{3}$ units.

→ But, Scattering ~ greater than would be accounted

- **Measured temp. of bulk liquid ≠ Actual temp. of the surface where growth was observed**
- **Growth at a free surface may differ from that in the liquid in an inverse way to that of growth on a solid substrate.**



ΔT = 0.4 ~ 11

Observation of the disturbance to the surface of a supercooled bath of thin by growing dendrites.

Fig. 4.17. Rate of growth of tin crystals in supercooled liquid tin.

c) Orrok's measurement of Tin : Observation within the bulk rather than at the surface

Timed the rise of the temperature at two points in the melt, observed from the output of thermocouples connected to an oscilloscope circuit.

⟶ **Considerable scattering, but differ considerably from those of (b) Fig 4.17**

"Growth in solid substrate at the same ΔT faster than free growth case"

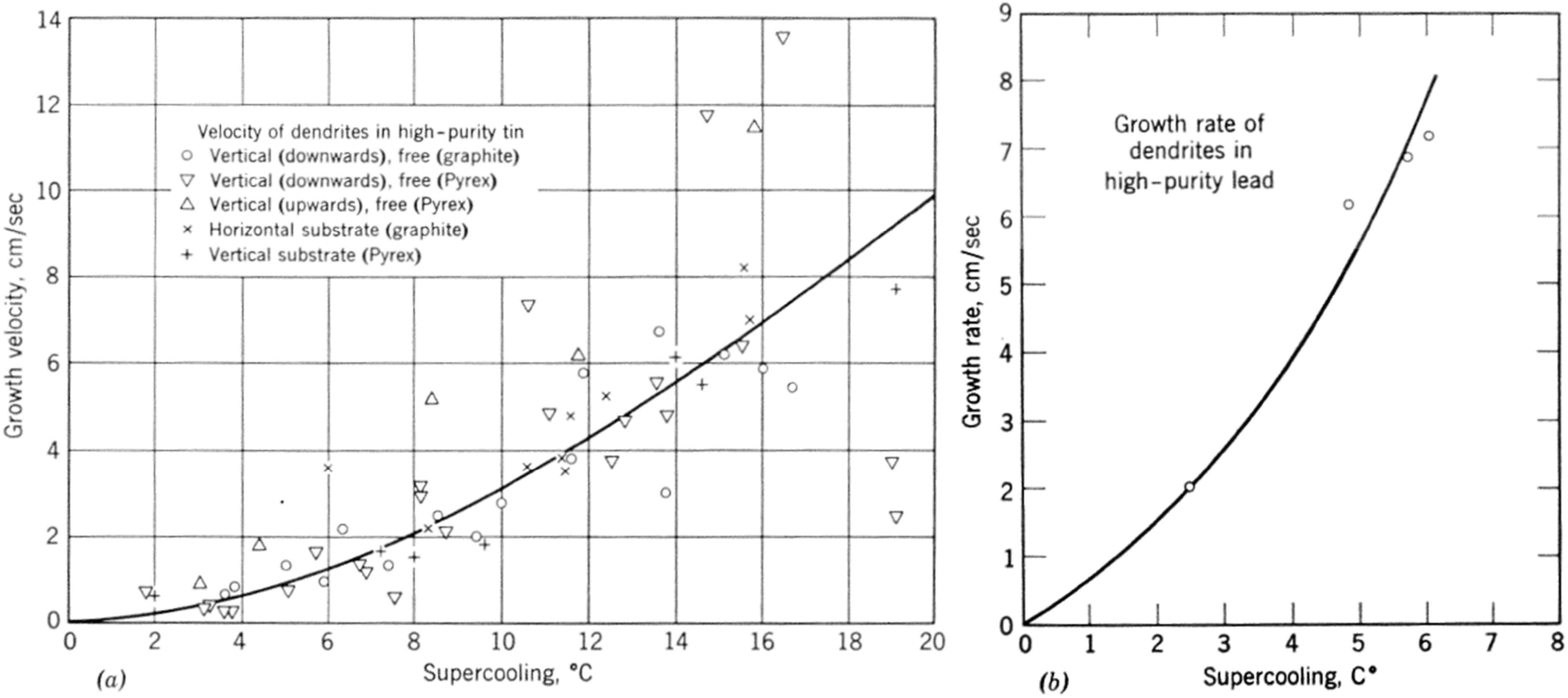


Fig. 4.18. Rate of growth of tin crystals in supercooled liquid tin and lead.

d) Lindenmeyer

: Extensive measurements on the growth of ice in supercooled water, using visual observation of the dendrites growing vertically downwards in a glass tube.

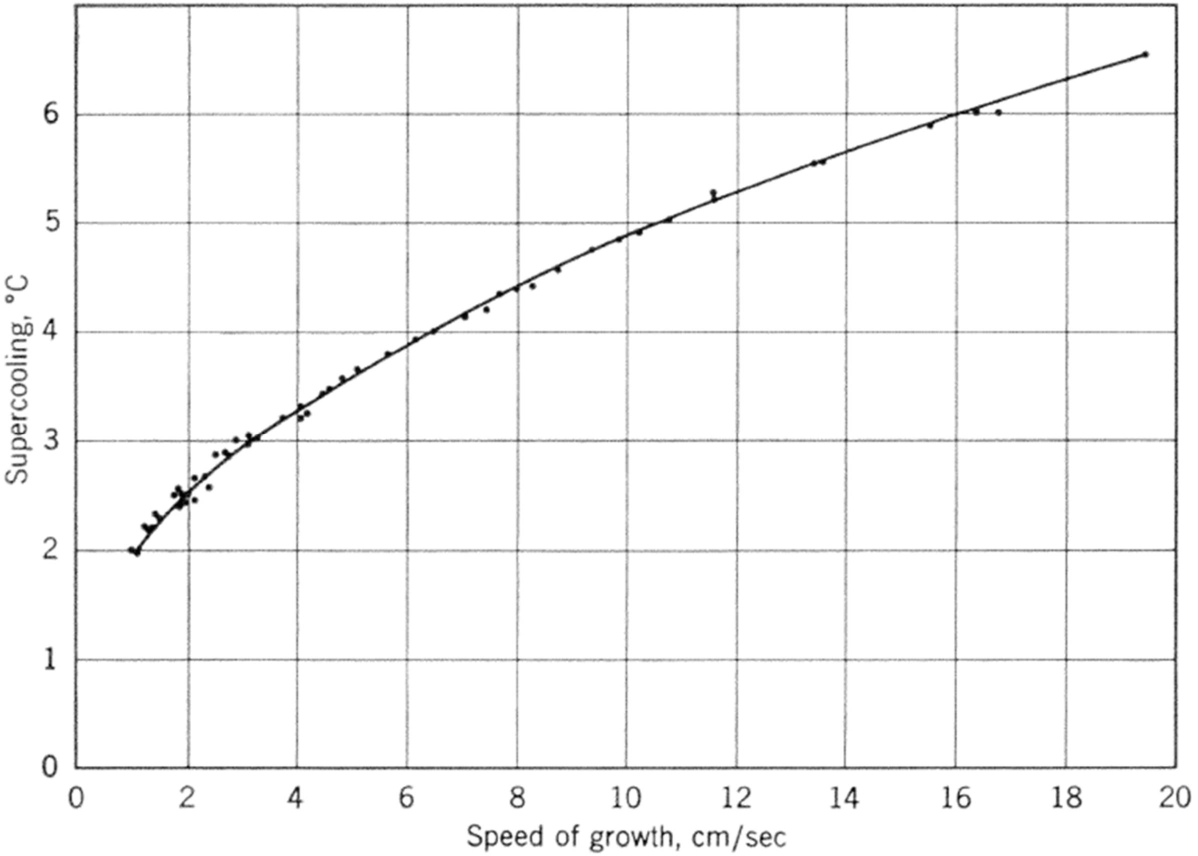
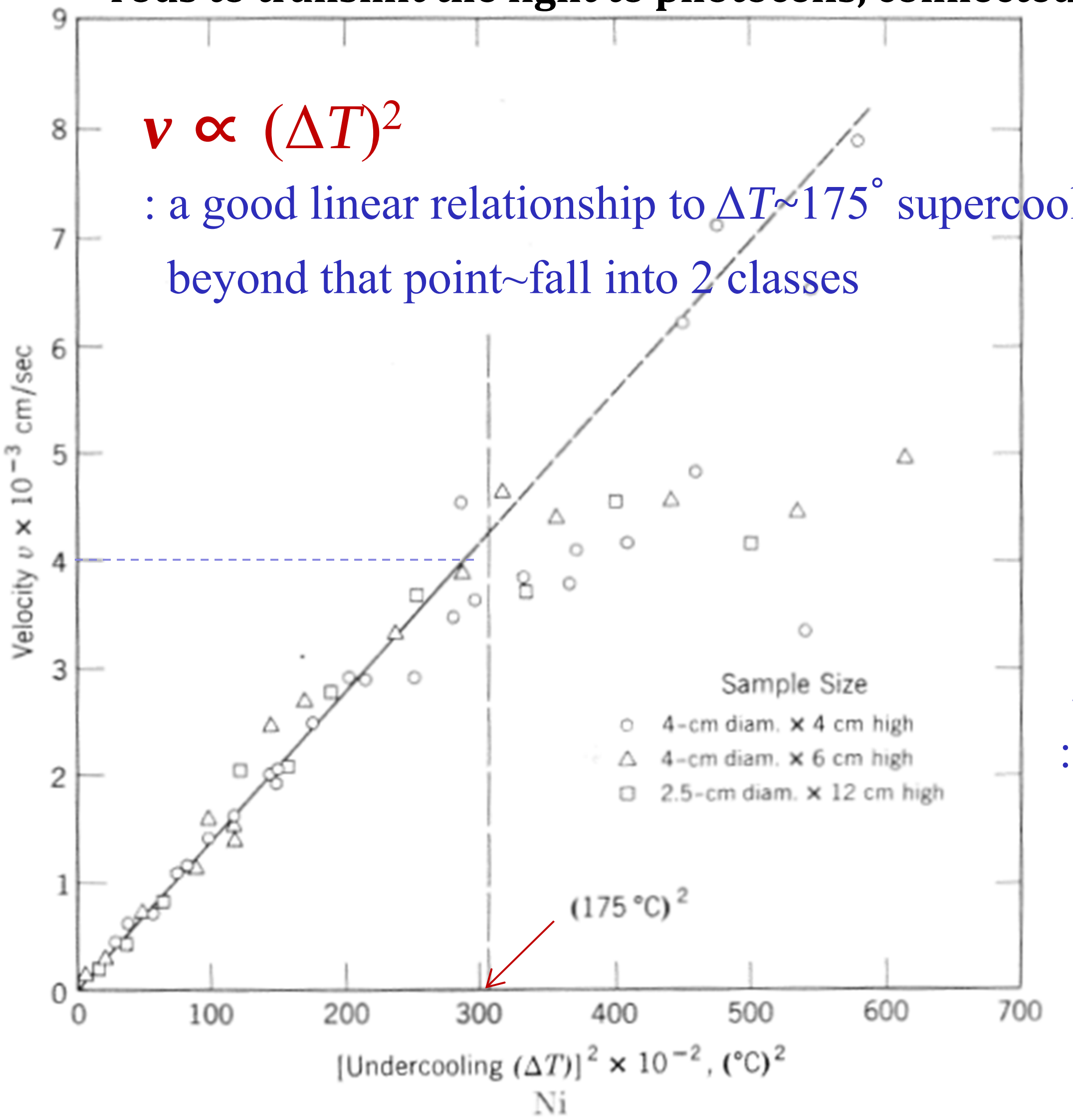


Fig. 4.19. Rate of growth of ice in supercooled water

e) Walker less scatter and cover a larger range of supercooling ΔT

: Extensive measurements on the growth of dendrites in nNi and Co, both of which he has succeeded in cooling in bulk (400 gm) to the homogeneous nucleation temp.

~ observed time interval btw recalescence at two points in the melt using quatz rods to transmit the light to photocells, connected to an oscilloscope



$v \propto (\Delta T)^2$

: a good linear relationship to ΔT~175° supercooling;

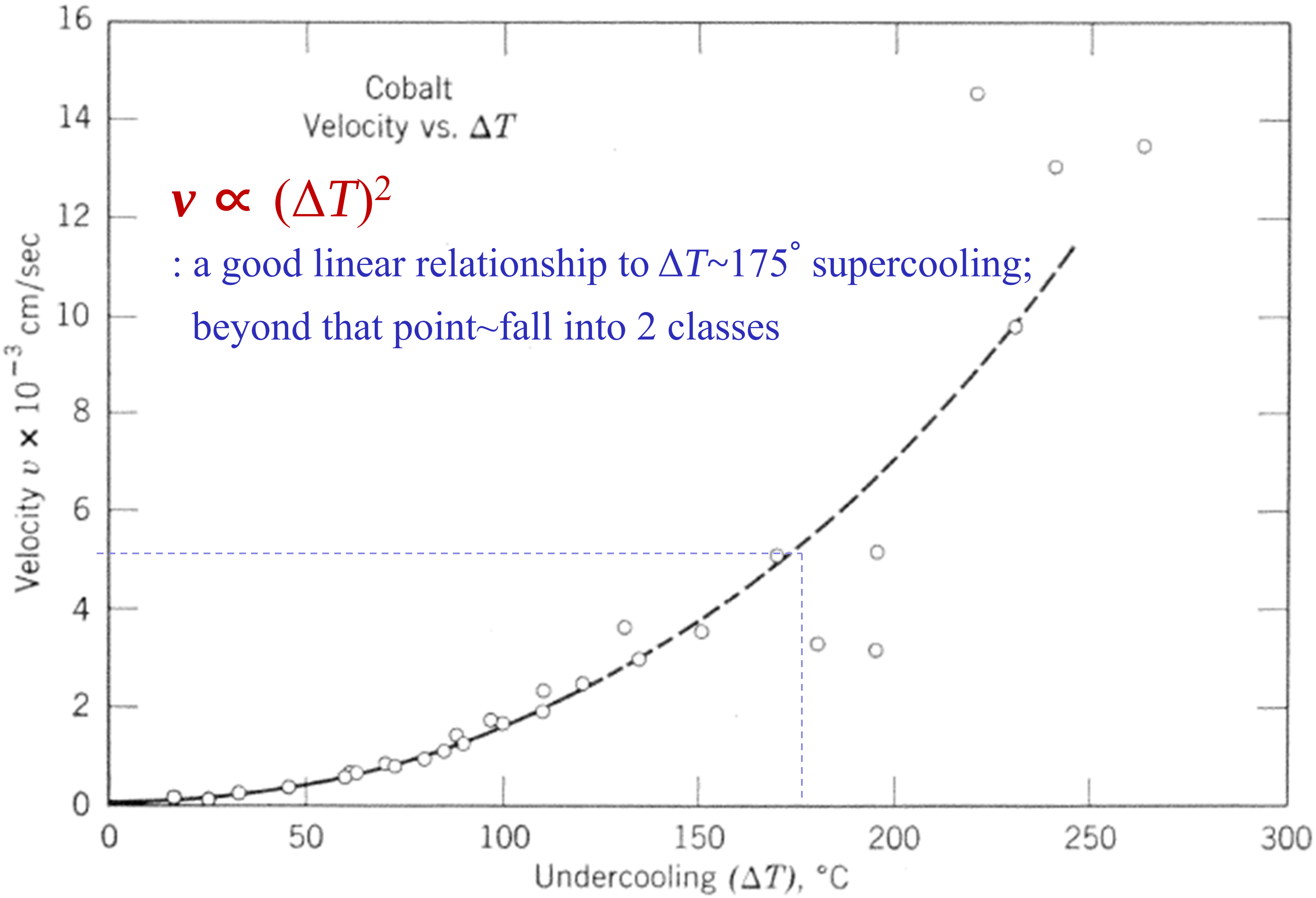
beyond that point~fall into 2 classes

Fig. 4.20. Rate of growth of nickel in undercooled melt

3 different sizes of specimen

: surface growth accelerated by heat transfer to the container is not influencing the result significantly.

∗ Similar characteristics for cobalt



$v \propto (\Delta T)^2$

: a good linear relationship to ΔT~175° supercooling;

beyond that point~fall into 2 classes

Fig. 4.21. Rate of growth of cobalt in undercooled melt

f) Colligon and Bayles:
Growth velocity measurements on Ni

by a method using optical fibers
to transmit the light due to
recalescence to a photocell
(similar to the method used by Walker)
and by high speed photography
of the top surface of the melt

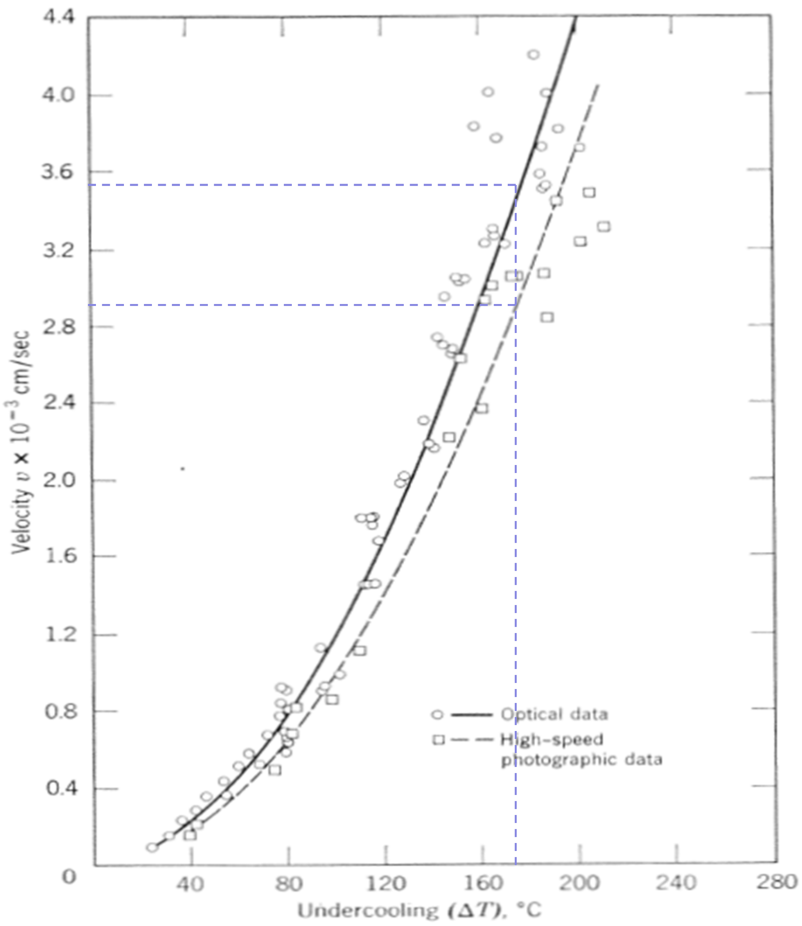


Fig. 4.22. Rate of growth of Nickel in undercooled melt

*** Experimental observations of the rate of growth of ribbon crystals of Germanium**

- **If measured tip radius is used, growth of Ge dendrite of the ribbon type can be accounted for quantitatively on the steady state theory of growth of a paravoloid of revelution.**
- **but, if kinetic driving force is neglected, this radius does not coincide with the value predicted on the maximum velocity criterion.**

∴ although the departure of the tip temp. from equilibrium is small, this difference has an important influence on the tip radius and on the rate of growth.

b) Non-steady state theory

Growth vs. branching of dendrite: periodicity of process

→ overall control: by heat flow into a colder liquid ~ unchanged

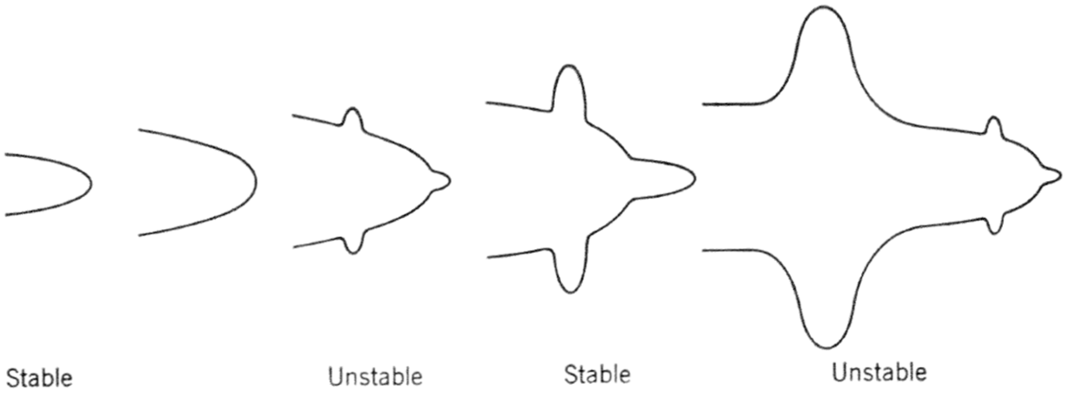


Fig. 4.14. Branching of dendrites.

∗ EXPERIMENTAL OBSERVATION OF RATE OF DENDRITIC GROWTH

(1) Growth in solid substrate at the same ΔT faster than free growth case

(2) lead dendrite grew much faster than the smooth interface

(3) R data: Scattering
(∵ Dendrites, which were nucleated by local cooling of the melt, grew with random orientations)

(4) $v \propto (\Delta T)^2$: a good linear relationship to ΔT~175° supercooling;beyond that point~fall into 2 classes

(5) Although the departure of the tip temp. from equilibrium is small, this difference has an important influence on the tip radius and on the rate of growth.
(growth rate ∝ temp gradient & radius)

(C) Direction of dendrite growth

a) Weinberg and Chalmers

: the arms of dendrites always grow in crystallographically determined directions, each of which is the axis of a pyramid whose sides are the most closely packed planes with which a pyramid can be formed (this excludes the basal plane in the hexagonal structure)

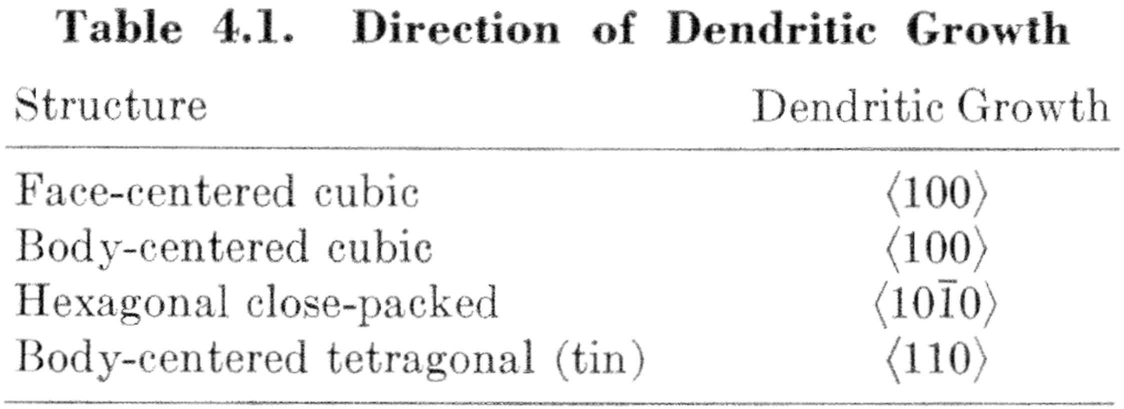


Table 4.1. Direction of Dendritic Growth

Structure	Dendritic Growth
Face-centered cubic	⟨100⟩
Body-centered cubic	⟨100⟩
Hexagonal close-packed	⟨10$\bar{1}$0⟩
Body-centered tetragonal (tin)	⟨110⟩

- According to these generalizations, the “dendrite arms” should always be orthogonal in the cubic and tetragonal and should form angles of 60° for the hexagonal close-packed metals.

- These rules are always fulfilled when the dendrites are exposed by decanting the liquid from a melt in which dendrites are growing; however, dendrites are often seen at a surface, either a free surface or one that was, during solidification, in contact with a mold wall. → “Growth direction change”

- In such cases, the arms are not always orthogonal in the cubic and tetragonal
  ∵ surface seen at the surface represents the intersection with the surface of the three sets of cube planes, in the case of a cubic structure.

* A example of a “non-orthogonal” dendritic structure in an aluminum alloy

When a dendrite arm reaches a surface, and cannot grow farther, its branches in the two orthogonal directions grow instead; they branch parallel to the original arm, as a series of branches that meet the surface at its intersection with the appropriate {100} planes.

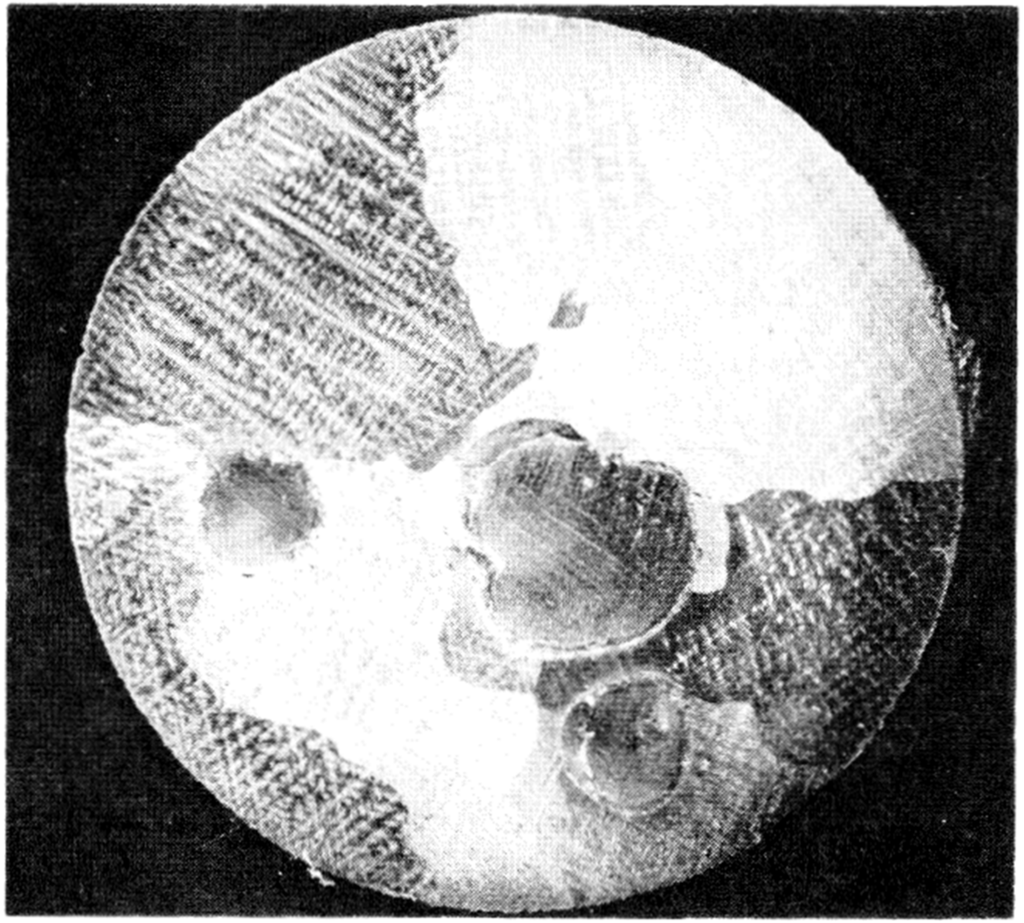


Fig. 4.23. Non-orthogonal growth of dendrite structure

* The general explanation for the crystallographic features of dendritic growth must be related to anisotropy of the relationship between growth rate and kinetic driving force.

1) If there were no anisotropy:

Dendrite should growth in a direction that is controlled entirely by thermal conditions

→ not clear in Fig. 4.24

2) If there were anisotropy:

(like Figure 4.24)

Characteristic directions are quite differently related to the heat flow pattern in the left and right halves of the specimen.

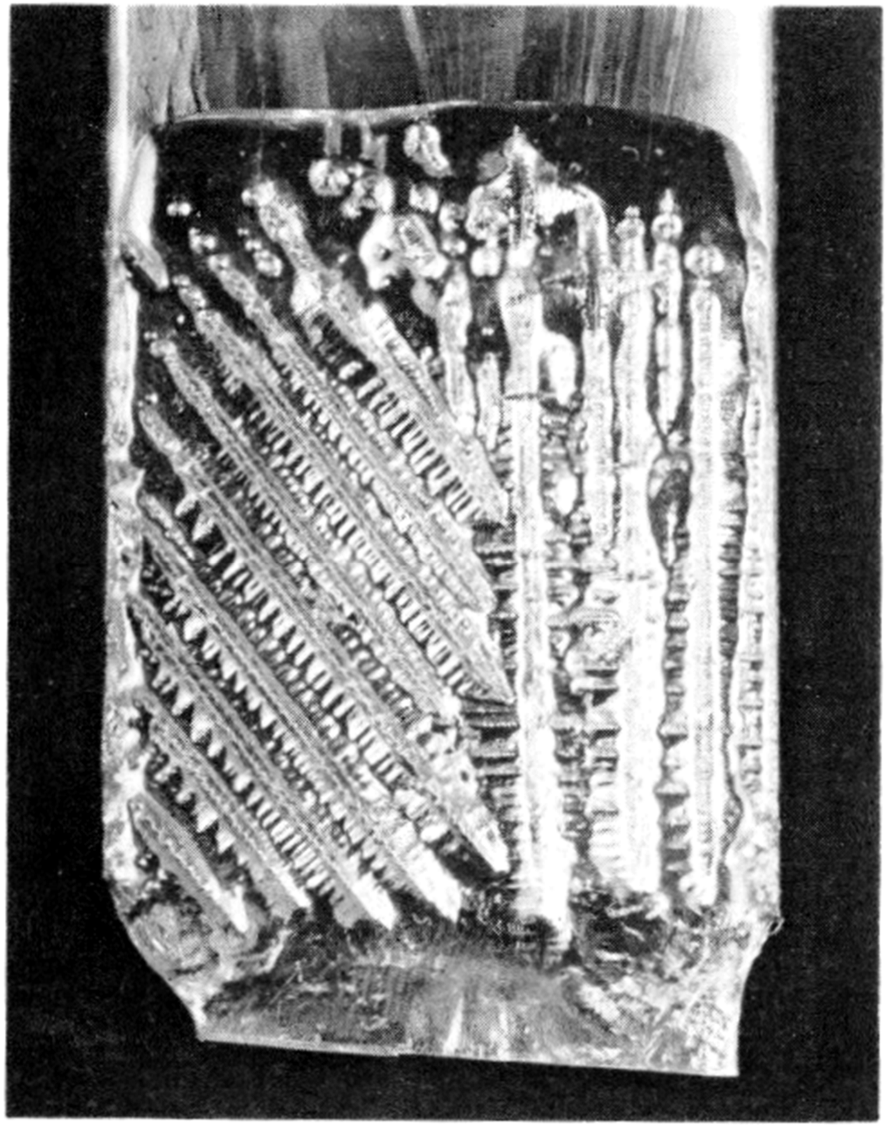


Fig. 4.24. Independence of growth direction and thermal conditions.

* The observed habit in FCC crystals would be accounted for if it could be shown that the growth rate, for a given ΔT, is greater for <100> directions than in <111> directions.

* Then the forward growth in a <100> directions would be restrained by the slower growth of the {111} planes that would form the sides of the pyramid truncated by a {100} plane as shown in Fig. 4.24.

* The “idealized” form of the dendrite (Fig. 4.25a) would not confirm to the heat flow conditions required for steady state growth, but the “rounded off” form (Fig. 4.25 b) would do so if a correction could be made for the slower growth (for a given ΔT) of the {111} faces than the {100} faces.

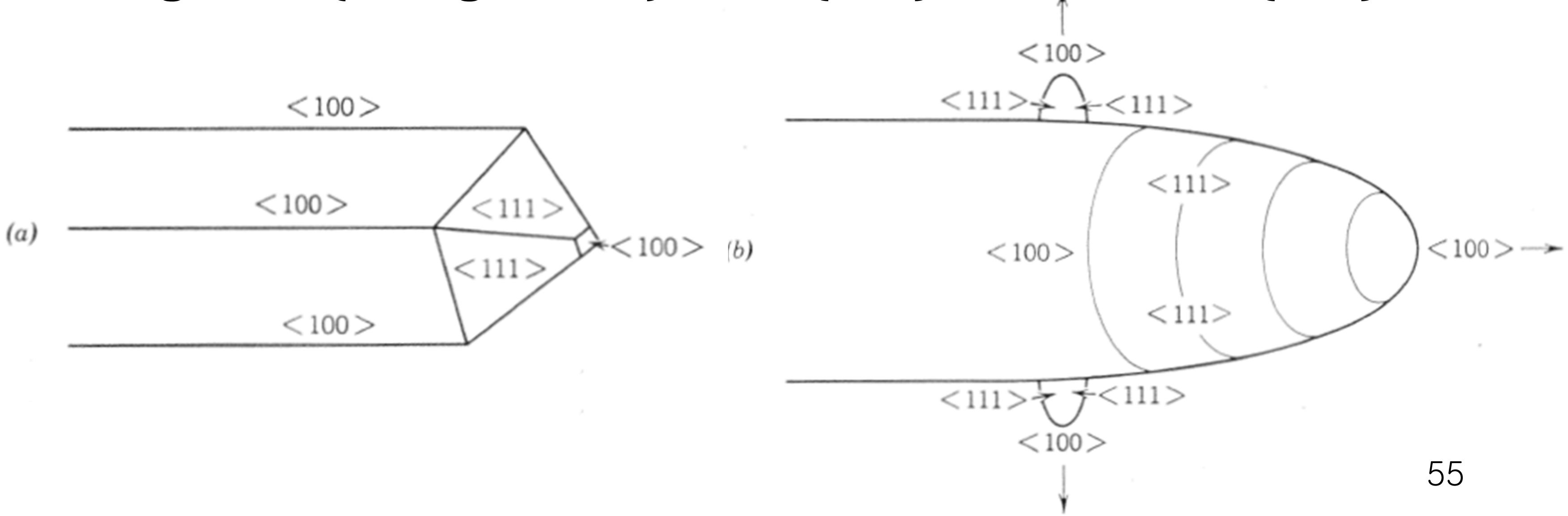


Fig. 4.25. Geometry of dendrite tip. (a) Schematic, (b) actual.

* The transition btw {100} and {111} faces is through high index or non-crystallographic sufaces that could, presumably, grow even faster than the {111} face at tip.

* The existence of some anisotropy in growth rate btw more and less closely packed faces is to be expected on the basis, proposed by Cahn that at low driving force, the surface of a metal, while diffuse, still grows by the lateral propagation of steps.

* But, there is, so far, no way of measuring the anisotropy of growth rate.

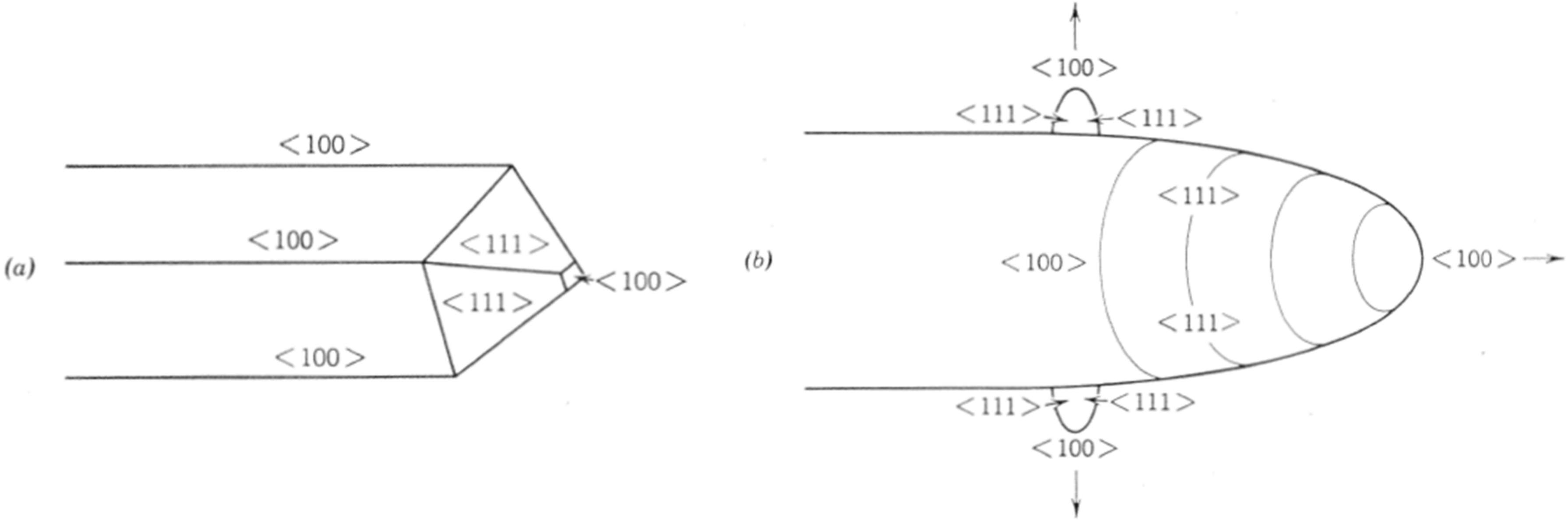


Fig. 4.25. Geometry of dendrite tip. (a) Schematic, (b) actual.

DIRECT OBSERVATION OF DENDRITE SHAPE

*** Spacing of dendrite arms**

Weinberg and Chalmer: ΔT ↑ → spacing of primary dendrite ↑

Increasing in spacing (qualitative explaination):
The region of the surface surrounding a developing instability have a smaller gradient of supercooling than regions that are undisturbed.

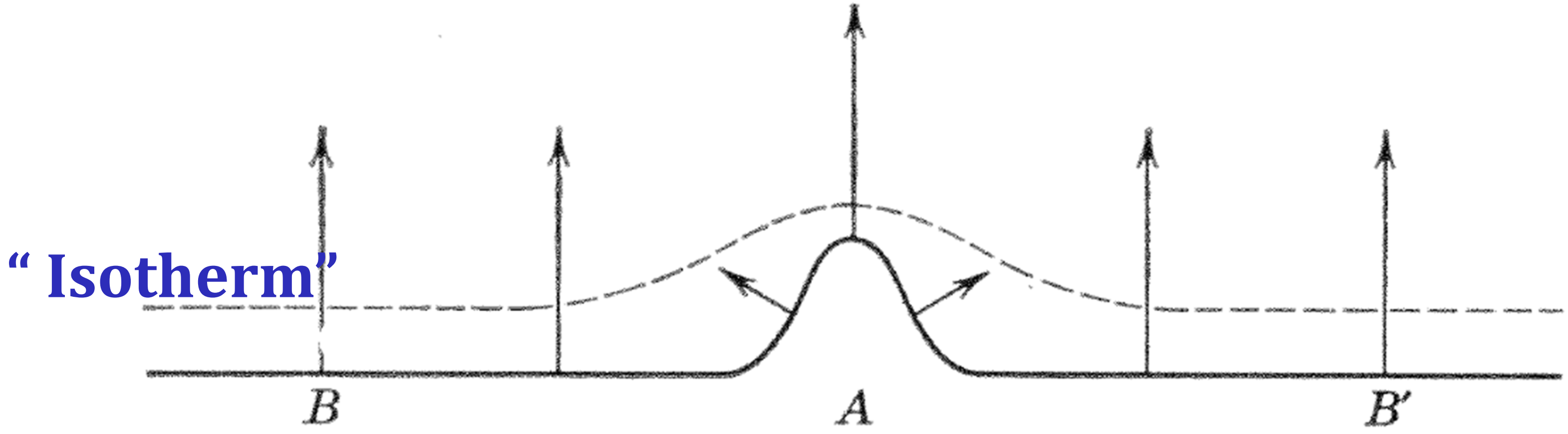


Fig. 4.26. Temperature distribution near a dendrite branch.

ΔT ↑ → Production rate of liquid ↑ → AB distance ↑
(the gradient is insufficient to allow arms to develop).

If the “instability” theory for dendritic growth is correct, then it would follow that the distance between successive positions of the tip at which instabililty developed would decrease as the ΔT in creased, and it would follow that the process proposed for the production of braches would be more closely spaced, because the critical radius is smaller for larger ΔT.

However, it is often observed that some branches are suppressed by their neighbors, and it is likely that the survival of branches, rather than their initiation, is controlled by the thermal process described above.

→ **There is as yet no satisfactory quantitative theory of branch spacing.**

Similar agreements would apply to the spacing of the branches that grow laterally from the main arms, and to the secondary and successive generations of braches.

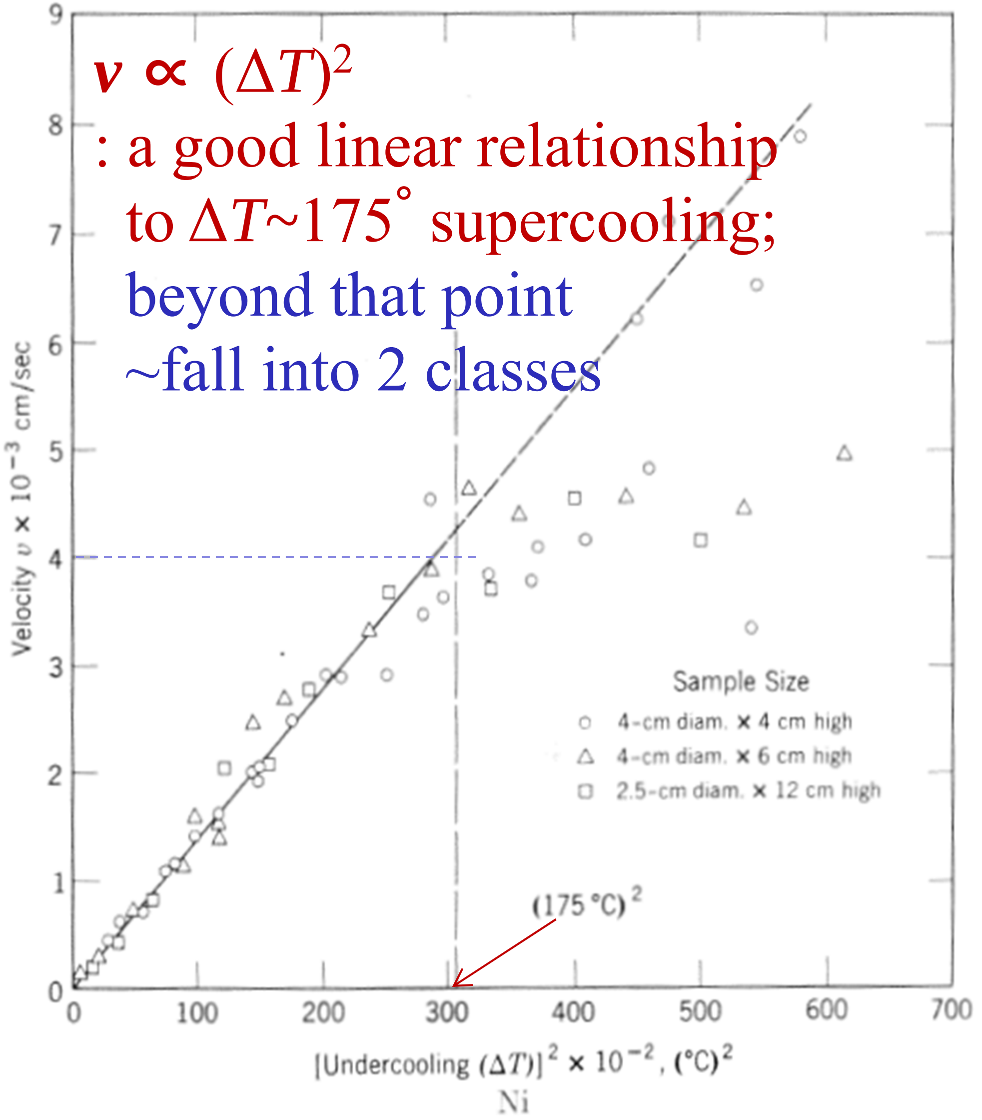
The experimental observation is that each successive generation is on a progressively finer scale, that is, thinner spikes more closely spaced.

This would correspond to the expected progressive decrease in the supercooling of the remaining liquid as growth proceeds.

→ **The branches on any individual arms are approximately, but not precisely, uniformly spaced.**

4.6. Solidification at very high supercooling: **ΔT > 175° Ni, Co**

: Reliable estimates of the grain-size characteristic of the high supercooling conditions could not be obtained without "dopping" the melt with a small addition of silver, which inhibits grain growth after solidification.



$v \propto (\Delta T)^2$

: a good linear relationship to ΔT~175° supercooling; beyond that point ~fall into 2 classes

Fig. 4.20. Rate of growth of nickel in undercooled melt

ΔT < 175° : a few crystal, typical grain size 1.5 cm

ΔT > 175° : typical grain size 0.01 cm

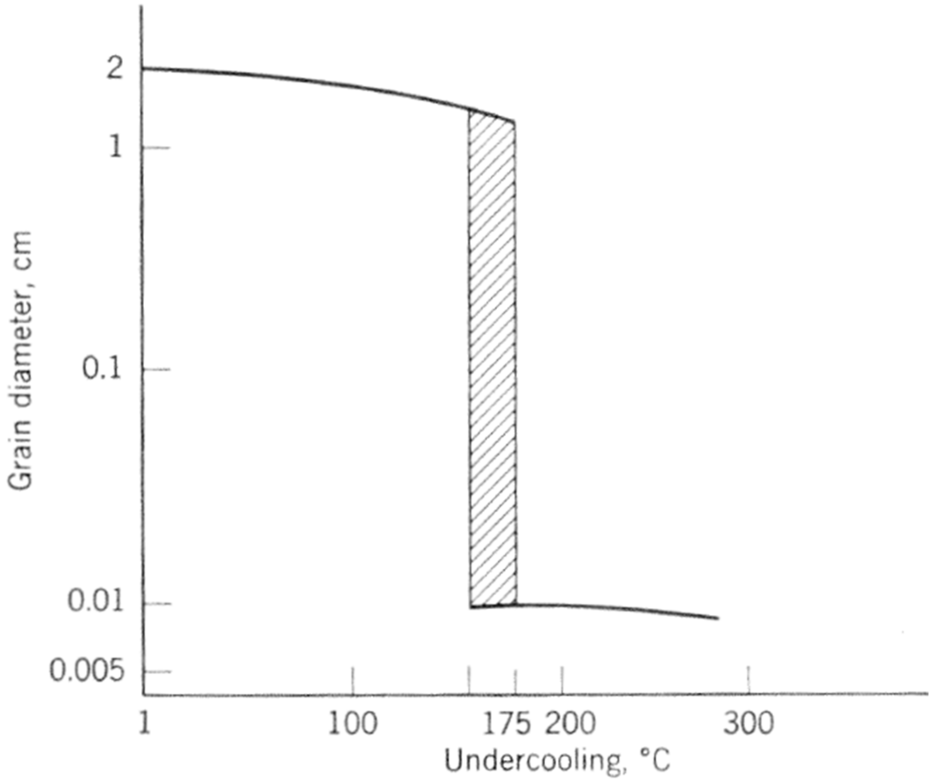


Fig. 4.27. Grain sized nickel as a function of undercooling (from Ref. 26.)

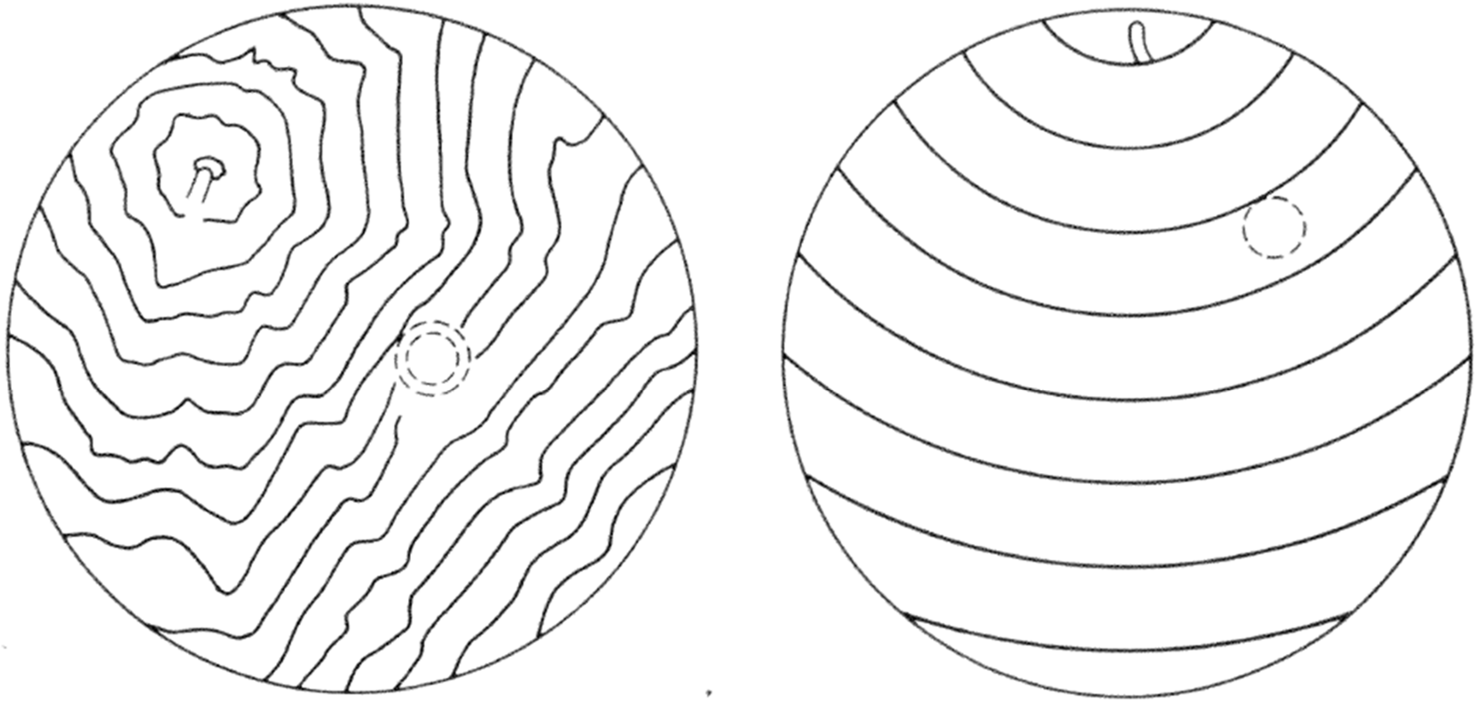
4.6. Solidification at very high supercooling: **$\Delta T > 175°$ Ni, Co**

$\Delta T < 175°$: low ΔT

a few distinct dendrite

$\Delta T > 175°$: high ΔT

Fine grain size
Smooth & continuous



(*a*) Angular interface
$\Delta T = 74°\,\mathrm{C}$

(*b*) Spherical interface
$\Delta T = 175°\,\mathrm{C}$

Fig. 4.28. Successive positions of the interface of nickel solidifying from (a) small supercooling, (b) large supercooling

ΔT > 175°C : high ΔT

Dendritic growth of existing crystals
→ Interrupted by the nucleation of new crystals
→ again interrupted by the formation of more crystals

ΔT < 175°C : low ΔT

Crystal size ~ $t^{1/2}$

→ the nucleation of new crystals at the surface of a sufficiently rapidly growing crystal & very large negative pressure can develop in the liquid adjacent to the growing crystal → cavitation → Nucleation

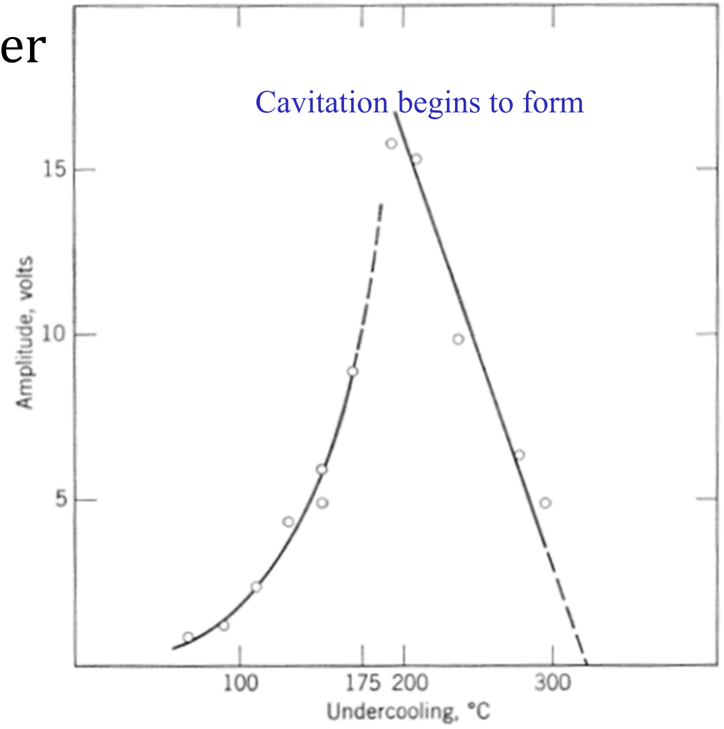
Condition for cavitation actually to occur is that the radius of the growing crystal should be above its critical nucleation radius (ΔT ~175°C) when the cavitation pressure reached.

As the crystal grows, the negative pressure passes through max. value.

Some interesting acoustical observations by walker

Apparent support to the cavitation theory of limiting dendrite speeds

→ **It is possible that the sound may be generated by the collapsing cavities; it is also possible that the sound is generated as the solid shrink away the mold wall.**



Cavitation begins to form

Fig. 4.29. Intensity of sound emitted during solidification as a function of supercooling

Mid term :

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Lecture notes 7

11/6   11 AM - 2 PM