

2020 Spring

Advanced Solidification

05.13.2020

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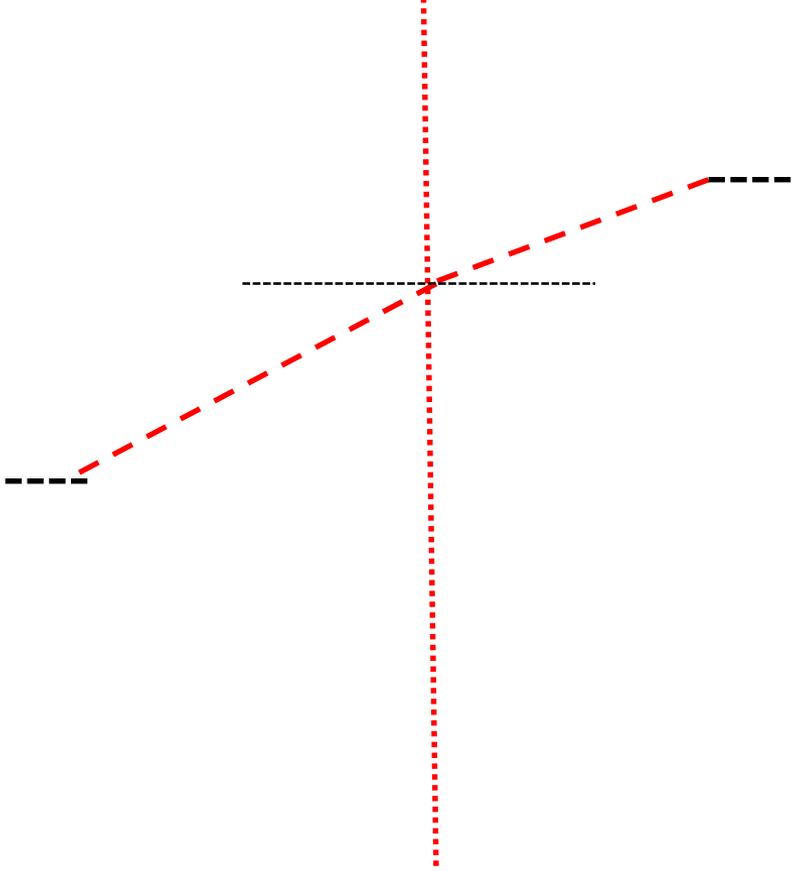
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Chapter 4. Microscopic Heat Flow Considerations

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

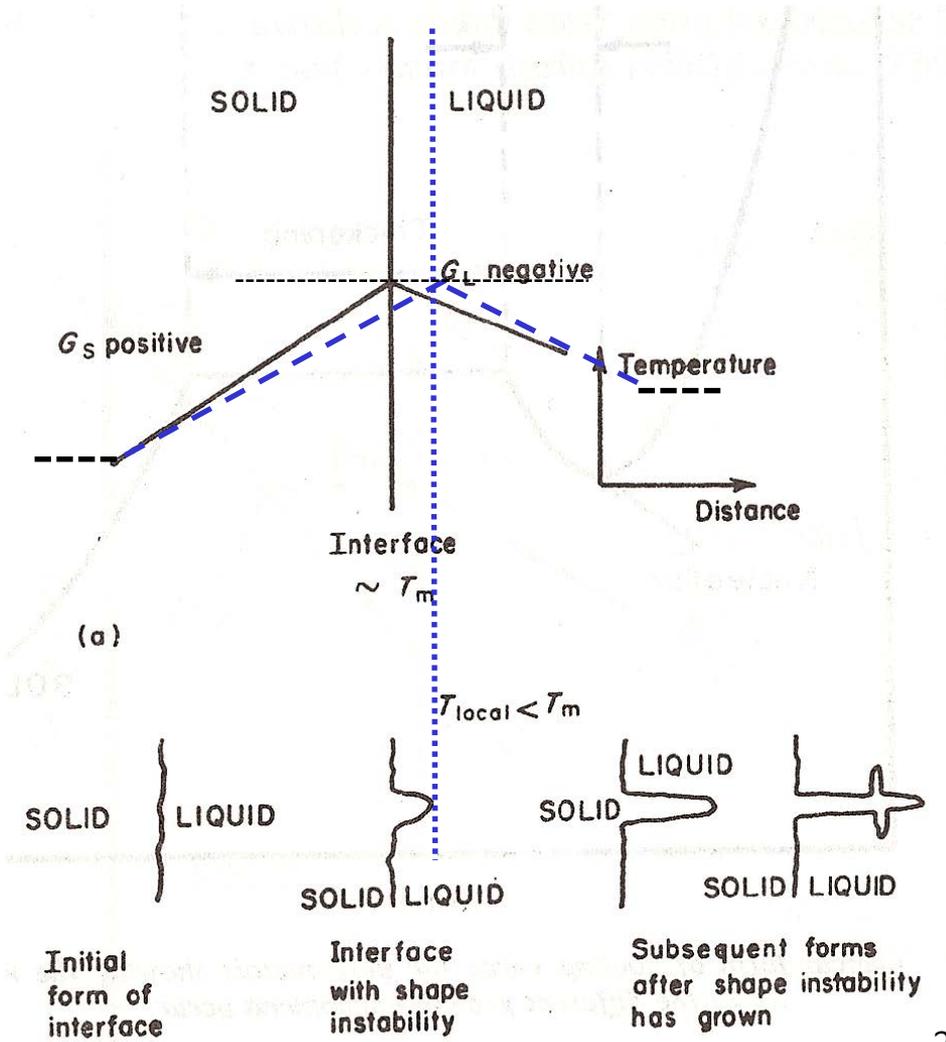
1) Superheated liquid

: Extraction of latent heat by conduction in the crystal



2) Supercooled liquid

: conduction of latent heat into the liquid

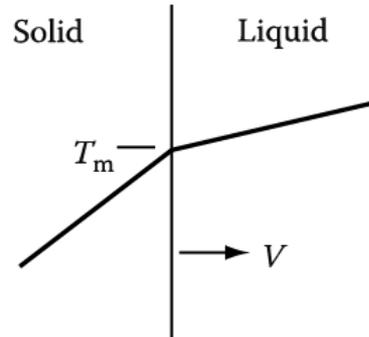


Heat Flow and Interface Stability - Planar interface

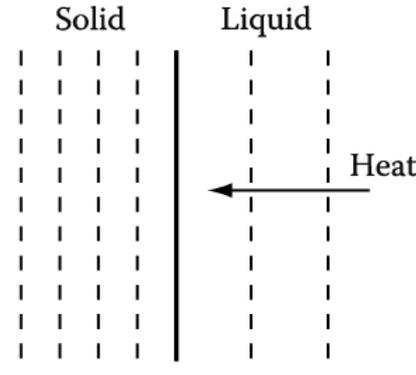
1) Superheated liquid: Extraction of Latent Heat by Conduction into the Crystal

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

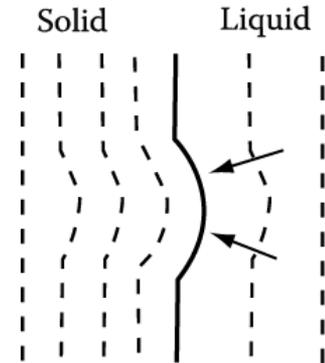
solid growing at v
(planar)



(a)



(b)



(c)

Heat flow away from the interface
through the solid

$$K_S T'_S$$



$$K_L T'_L$$

- 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 \rightarrow 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. $T'_L \uparrow$ & $T'_S \downarrow$

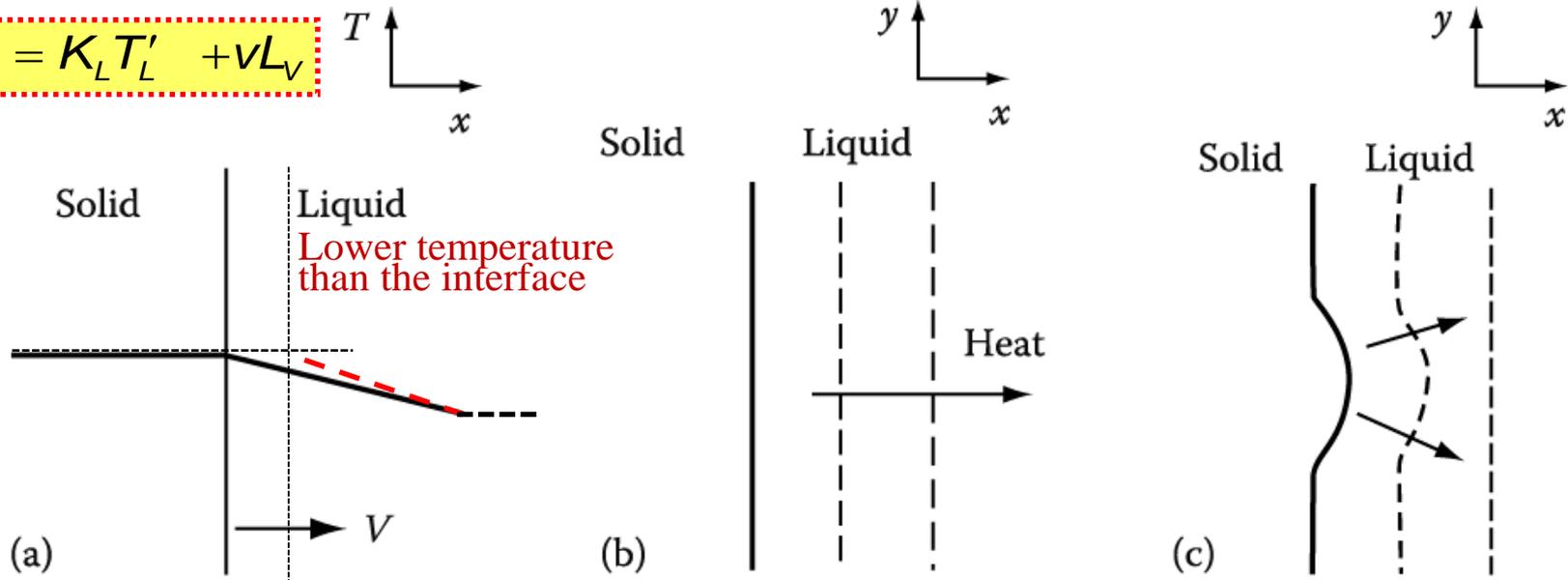
More heat to the protrusion \rightarrow melt away

v of protrusion \downarrow to match other v in planar region

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.

Effect of grain boundaries on S/L interface stability

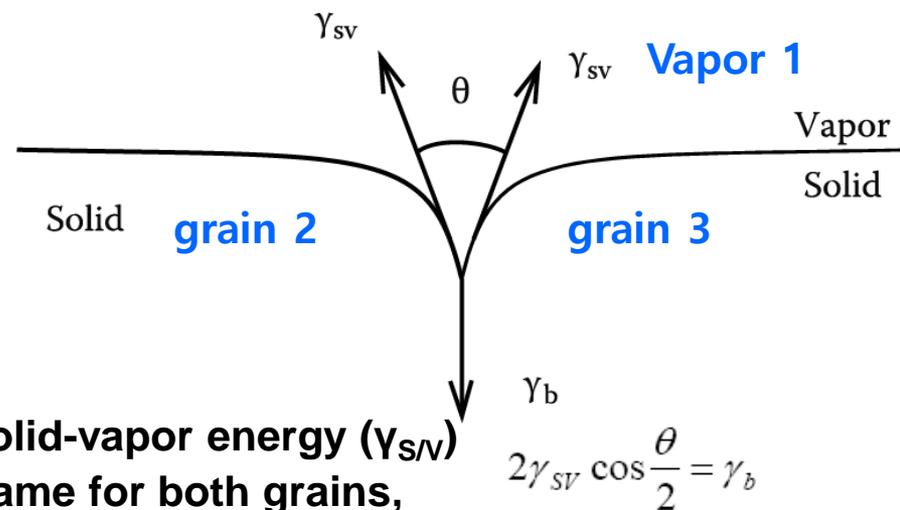
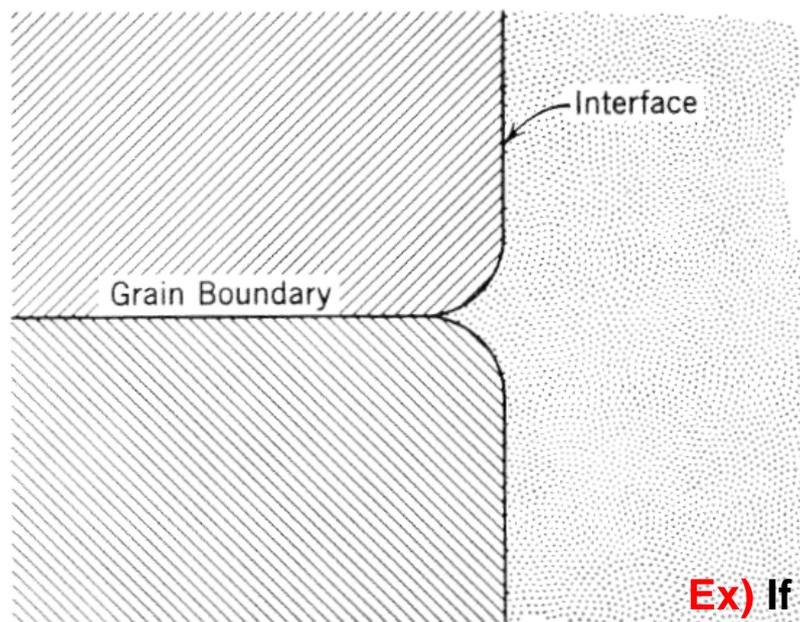
Grain boundary lies in the solid in a plane perpendicular to the solid-liquid interface.

→ 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.

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 (γ_{sv}) is the same for both grains,

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

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

(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

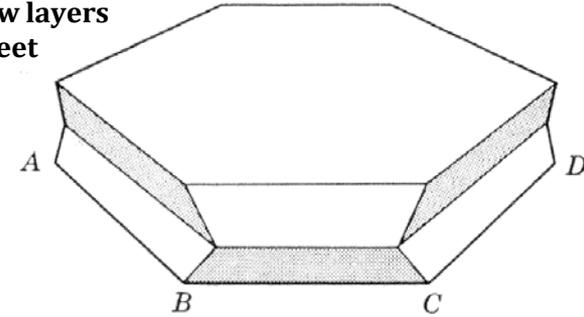
* Crystals of silicon, germanium, and bismuth

with a smooth interface under ordinary growth conditions

→ lateral growth/ orientation

“ re-entrant twin edge “

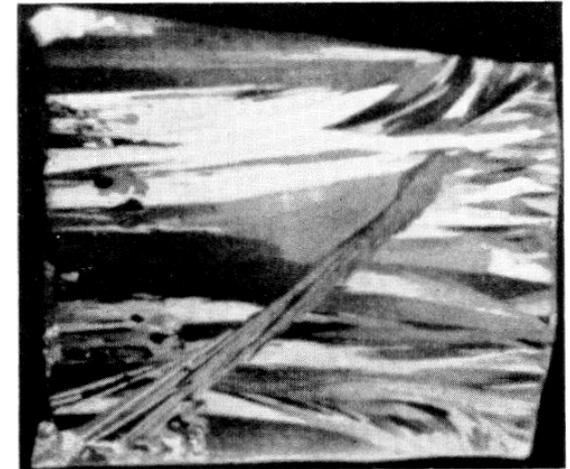
~ nucleation site for new layers
on the edges of the sheet



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 dendritically in basal plane of the structure and much more slowly, and with a flat interface, in perpendicular direction.

→ 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”

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



$$S \approx C \Delta T / L.$$

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

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

(2) Speed of growth

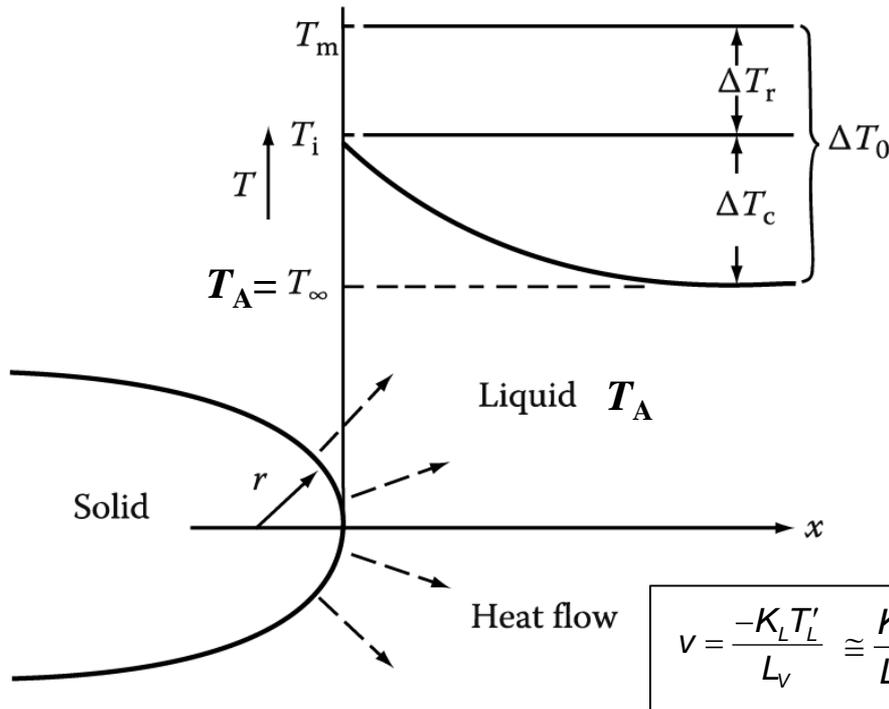
: depends on the shape and size of the tip and on its temperature

(a) Steady state theories

Assumption : a) tip ~ spherical and isotropic

of Fisher 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

$$v = \frac{2KL(T_E - T_I)}{2L\rho\sigma T_E} (T_I - T_A) \quad \boxed{\Delta T_r = \frac{r^*}{r} \Delta T_o}$$

$$= \frac{K}{\rho\sigma T_E} (T_E - T_I)(T_I - T_A) \quad \boxed{v \cong \frac{K_L}{L_v} \cdot \frac{\Delta T_c}{r} = \frac{K_L}{L_v} \cdot \frac{(\Delta T_o - \Delta T_r)}{r} = \frac{K_L}{L_v} \cdot \frac{\Delta T_o}{r} \left(1 - \frac{r^*}{r}\right)}$$

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, $\Delta T = T_E - T_A$)

$$\Delta T = T_E - T_A$$

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

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

* **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 ~ unreasonably 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 state conditions (i.e. at a constant velocity & constant shape). (r=tip radius)

$v \propto (\Delta T)^n / r$ $n \rightarrow 1.2$ for a paraboloidal dendritic of circular section to
Previously, $n \rightarrow 1$ $n \rightarrow 2$ 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 → $v_{max} \propto (\Delta T)$

(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

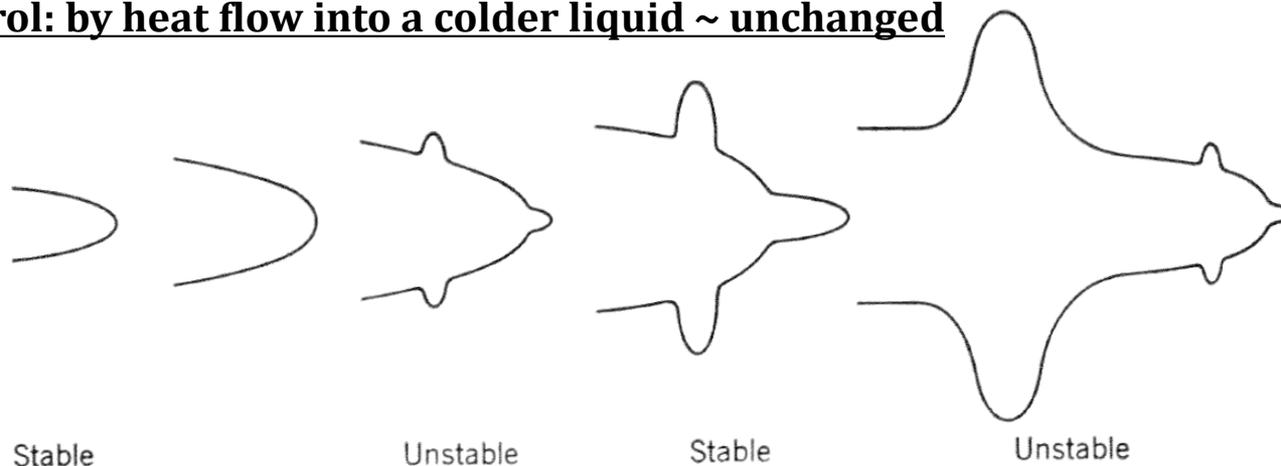


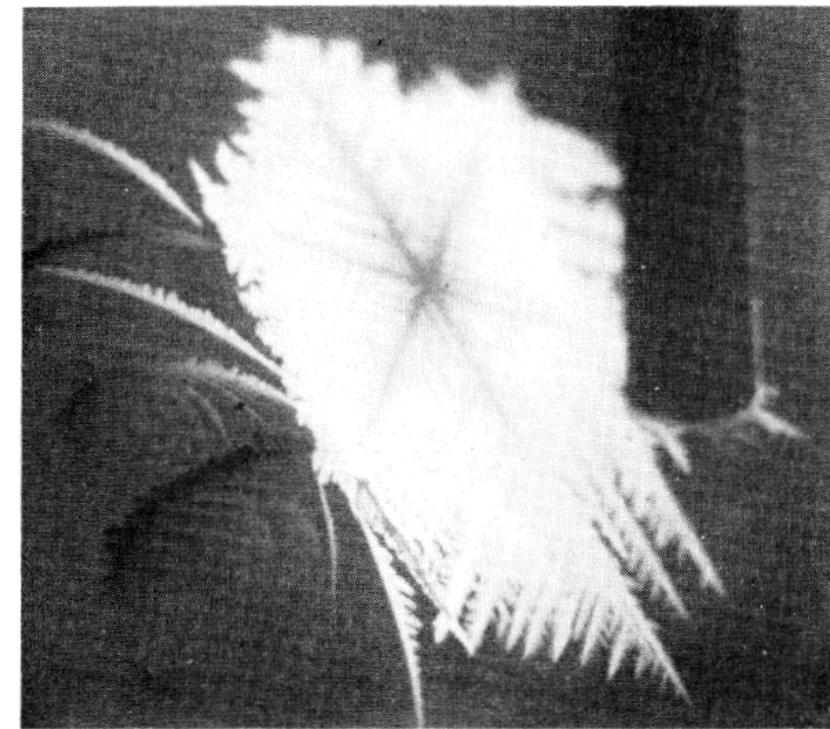
Fig. 4.14. Branching of dendrites.

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.

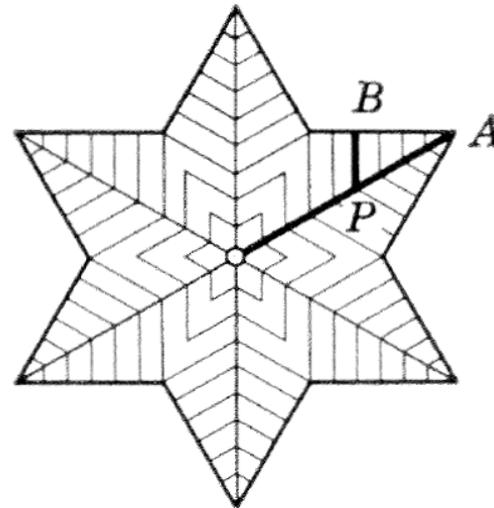
* $\overline{PB} < \overline{PA} \rightarrow v_{\overline{PB}} = v_{\overline{PA}} \rightarrow$ regular hexagon without re-entrant angles : Fig. 4.15. (c)

Secondary arm Primary arm

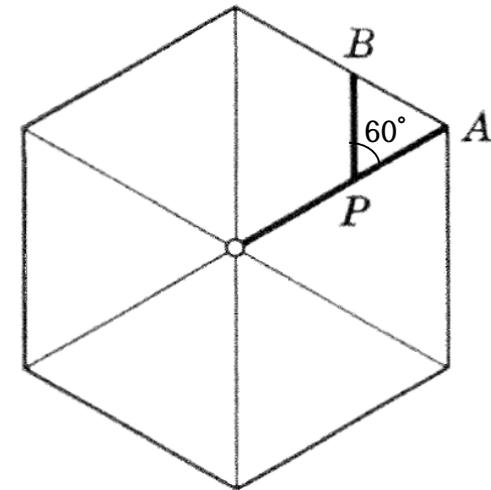
- Only difference between primary spike (\overline{PA}) and the secondary spike (\overline{PB}): \overline{PB} exhibit parallel array which is retarded by the thermal field of its neighbors.
- Speed ratio of free spike (\overline{PA}) and retarded spike (\overline{PB}) - PAB 60° angle
 → This angle is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



(a)



(b)



(c)

Fig. 4.15. Morphology of ice dendrites; (a) photograph of a dendrite, (b) schematic, (c) ideal ¹³

* Growth velocity of dendrite

A member of a row < a spike isolated dendrite

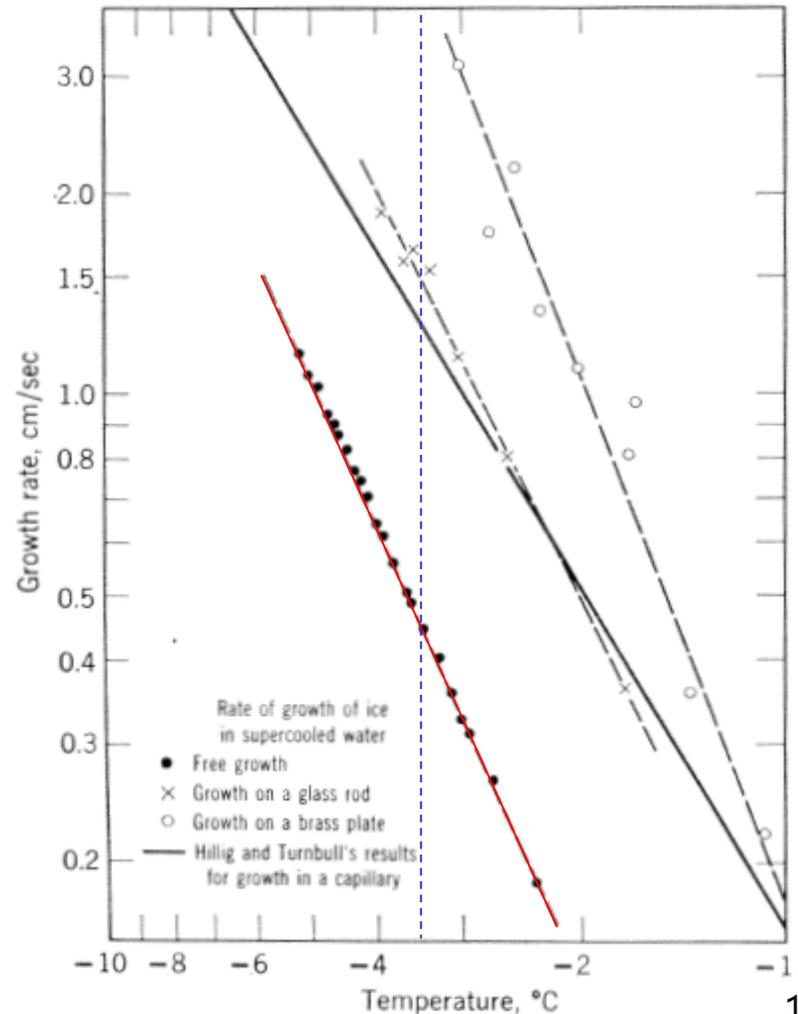
- Each dendrite of a 2D array will grow even more slowly as a result of their mutual interference by the overlapping of their thermal fields.

* 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 $\langle 111 \rangle$ direction would be $\sqrt{3}$ units.

→ But, Scattering ~ greater than would be accounted

- Measured temp. of bulk liquid \neq 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.

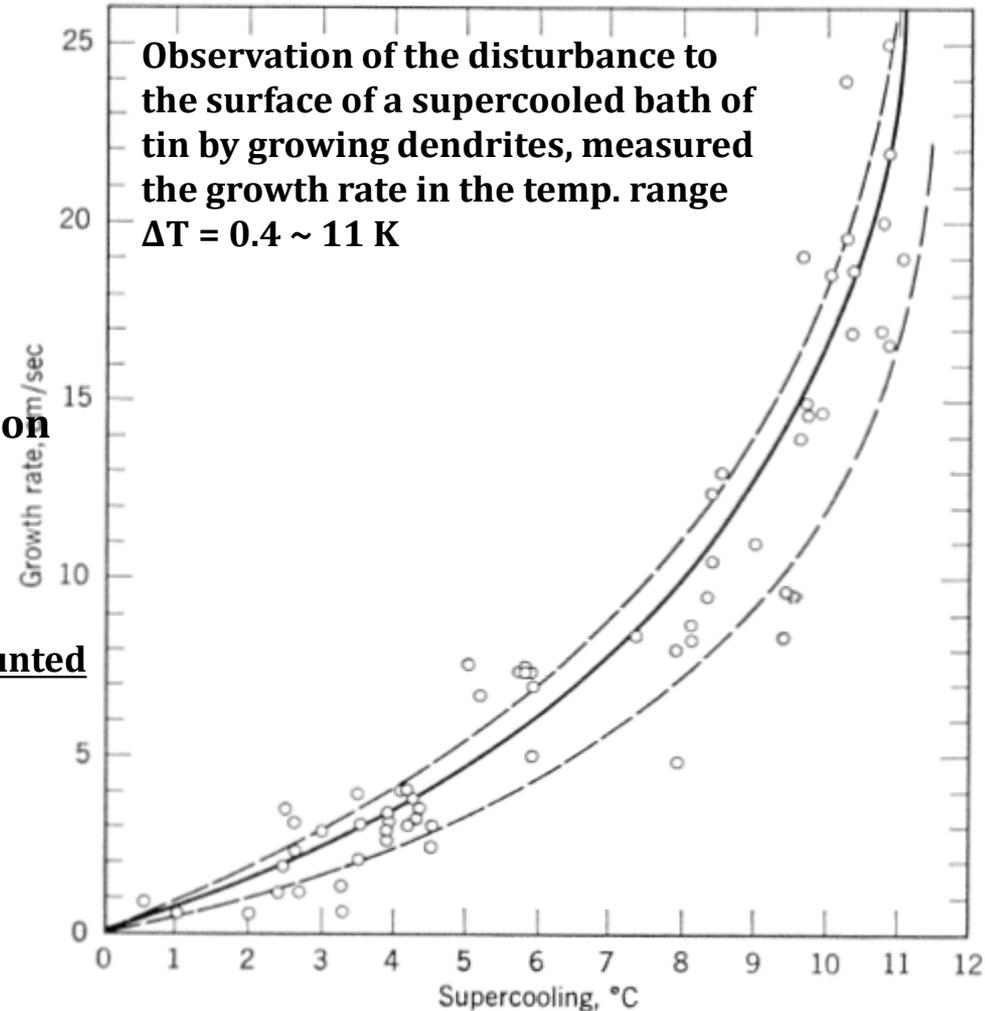


Fig. 4.17. Rate of growth of tin crystals in supercooled liquid tin.

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

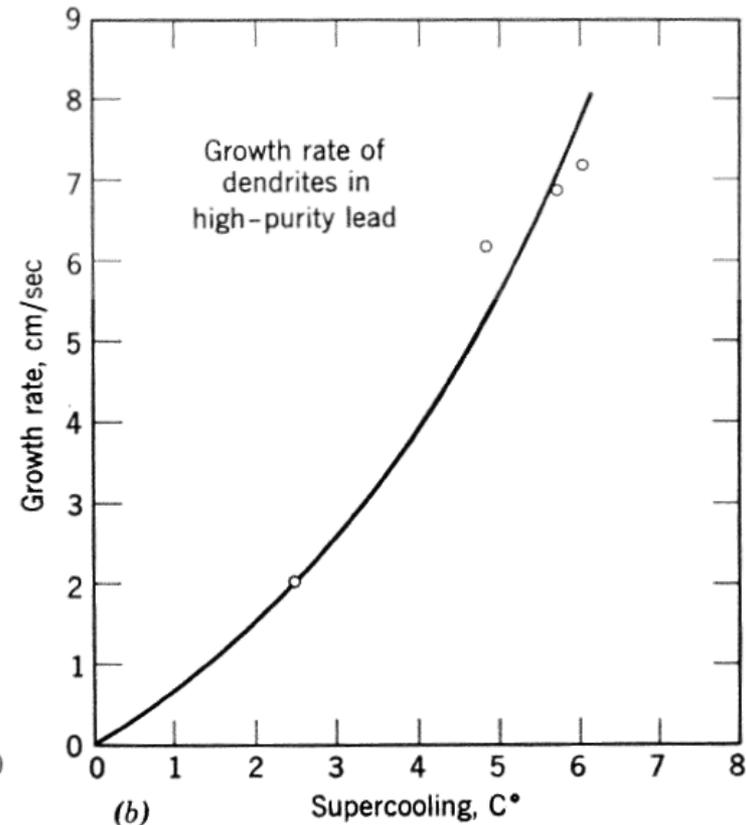
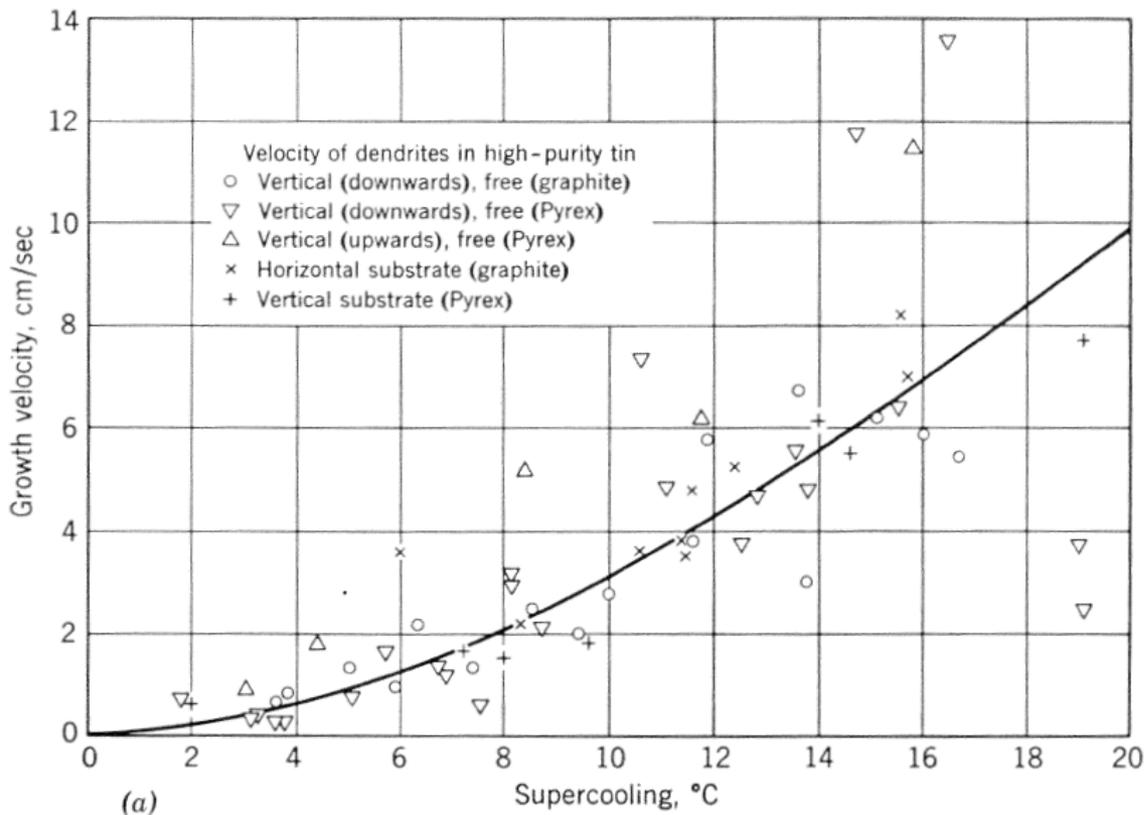


Fig. 4.18. Rate of growth of tin crystals in supercooled liquid tin and lead.

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.

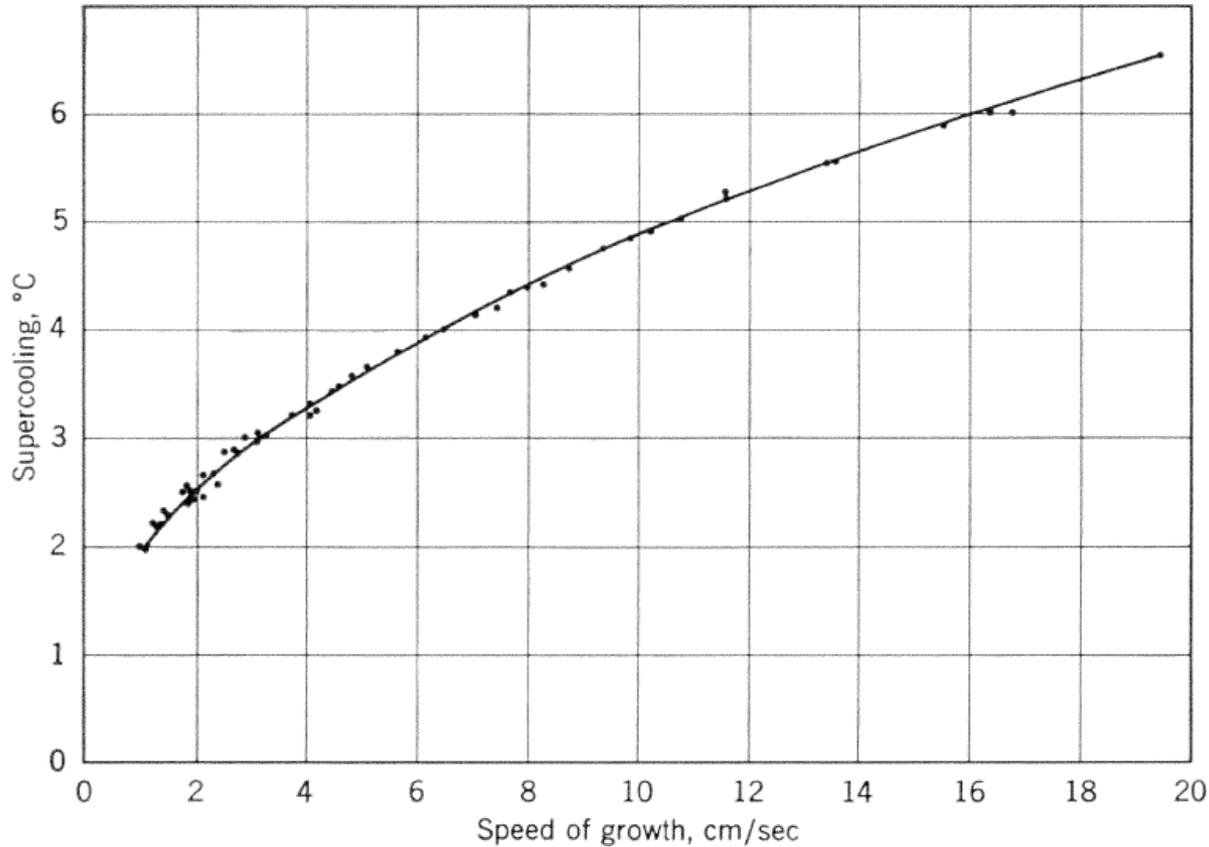
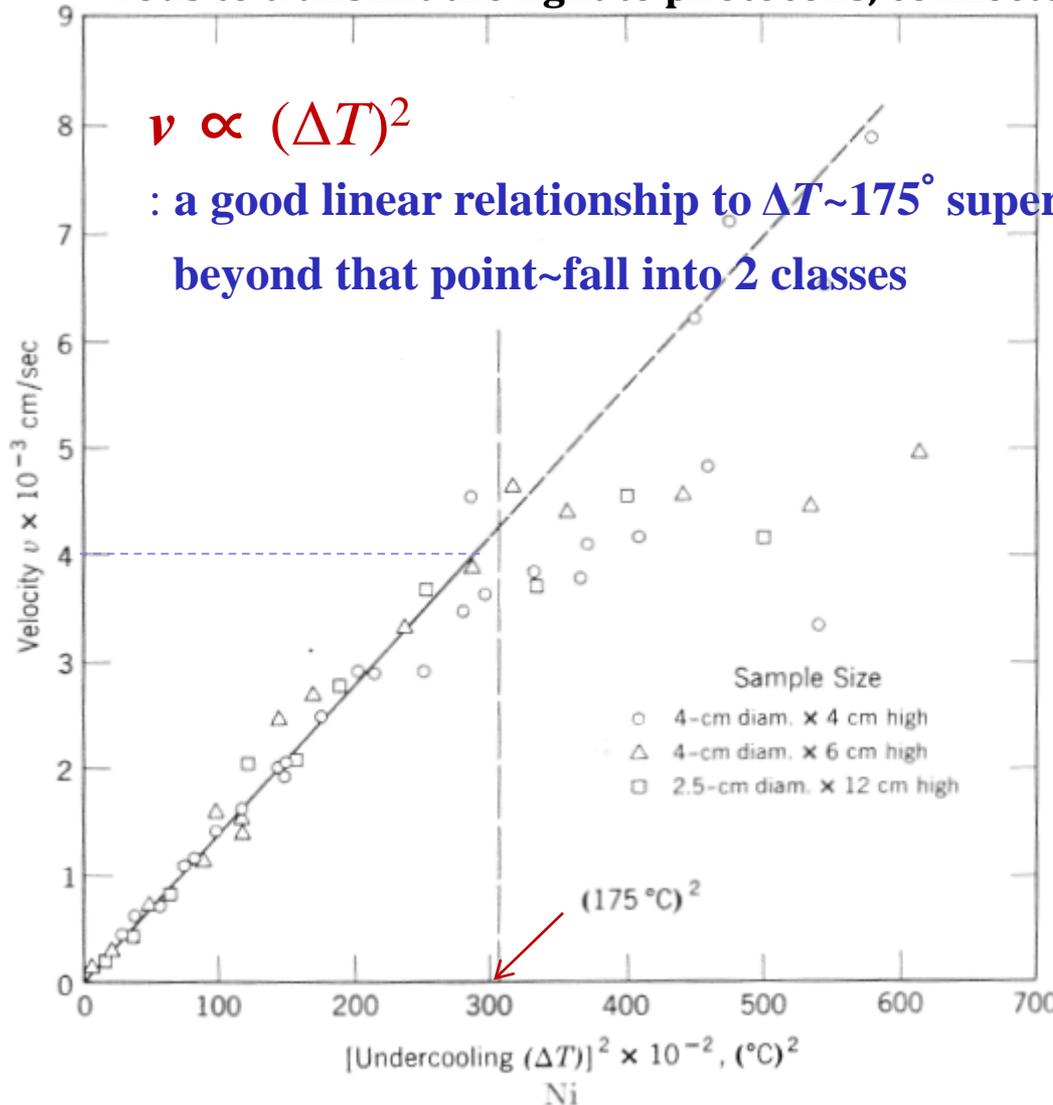


Fig. 4.19. Rate of growth of ice in supercooled water

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

: Extensive measurements on the growth of dendrites in Ni 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 quartz rods to transmit the light to photocells, connected to an oscilloscope



3 different sizes of specimen
: surface growth accelerated by heat transfer to the container is not influencing the result significantly.

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

* Similar characteristics for cobalt

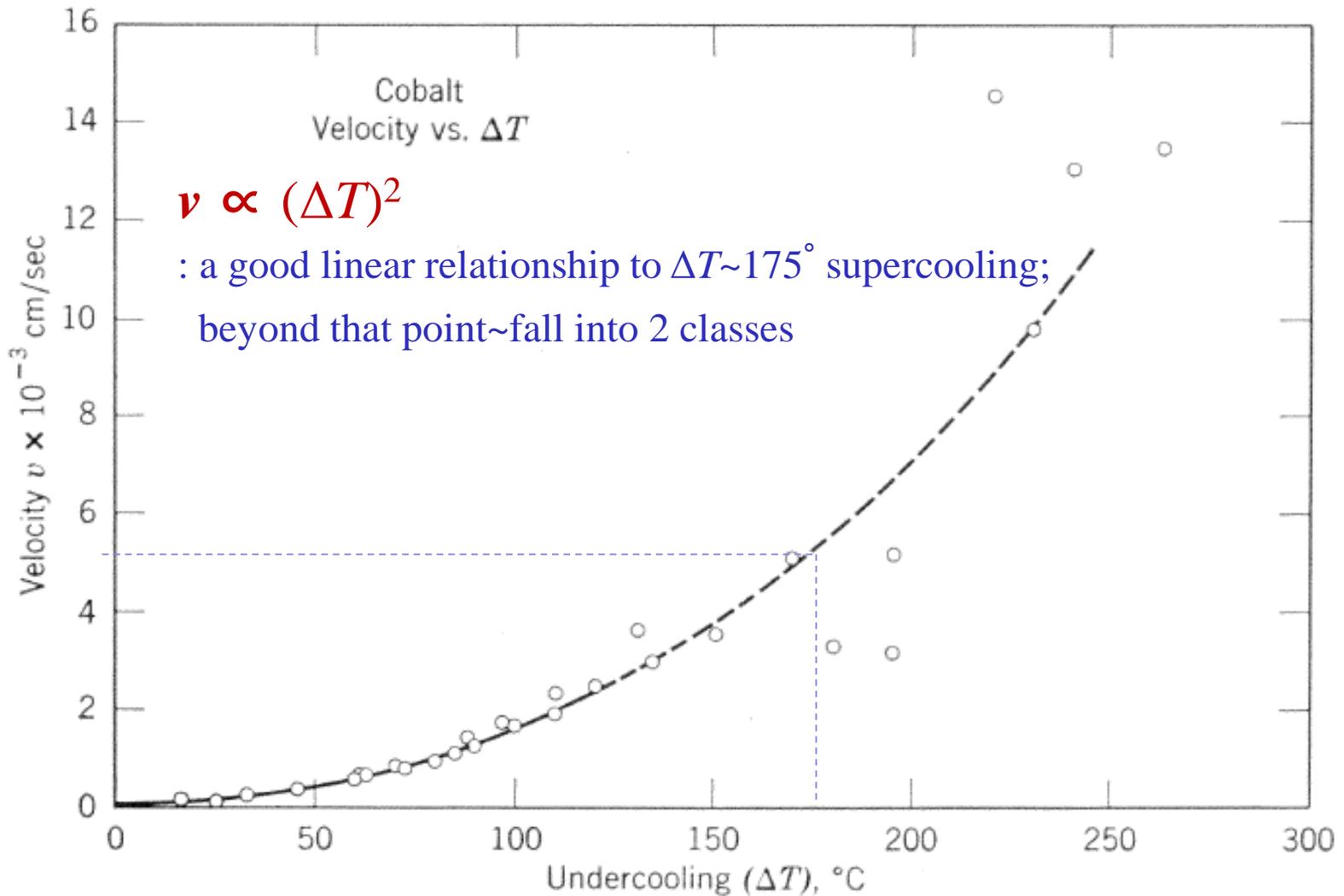


Fig. 4.21. Rate of growth of cobalt in undercooled melt

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

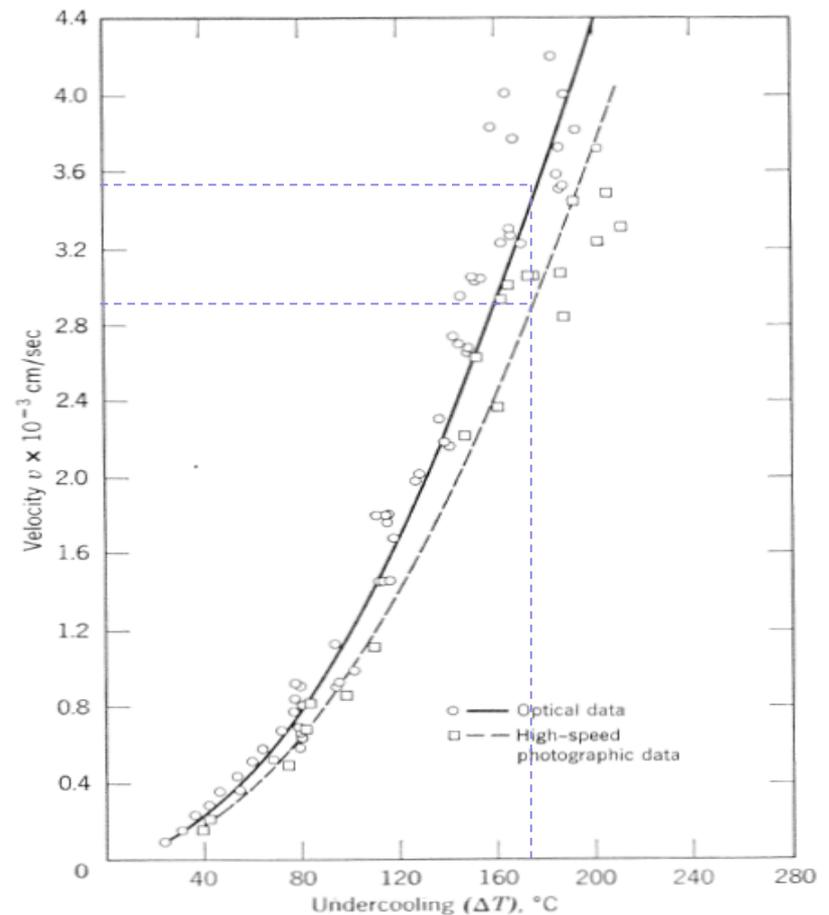


Fig. 4.22. Rate of growth of Nickel in undercooled melt

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

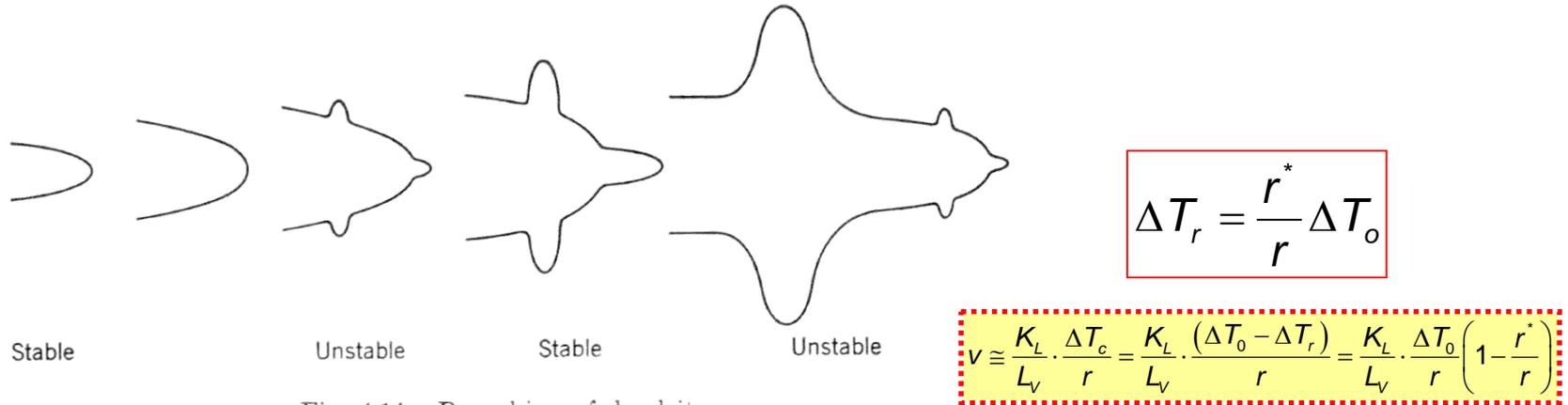
- If measured tip radius is used, growth of Ge dendrite of the ribbon type can be accounted for quantitatively on the steady state theory of growth of a paravoloid of revolution.
- but, if kinetic driving force is neglected, this radius does not coincide with the value predicted on the maximum velocity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



* 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 $\Delta T \sim 175^\circ$ 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, r and on the rate of growth, v .

(growth rate \propto temp gradient & radius)

IH: Please summarize one of the latest measurement methods for rate of dendritic growth (within 3 pages in ppt).

(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	$\langle 100 \rangle$
Body-centered cubic	$\langle 100 \rangle$
Hexagonal close-packed	$\langle 10\bar{1}0 \rangle$
Body-centered tetragonal (tin)	$\langle 110 \rangle$

- 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.

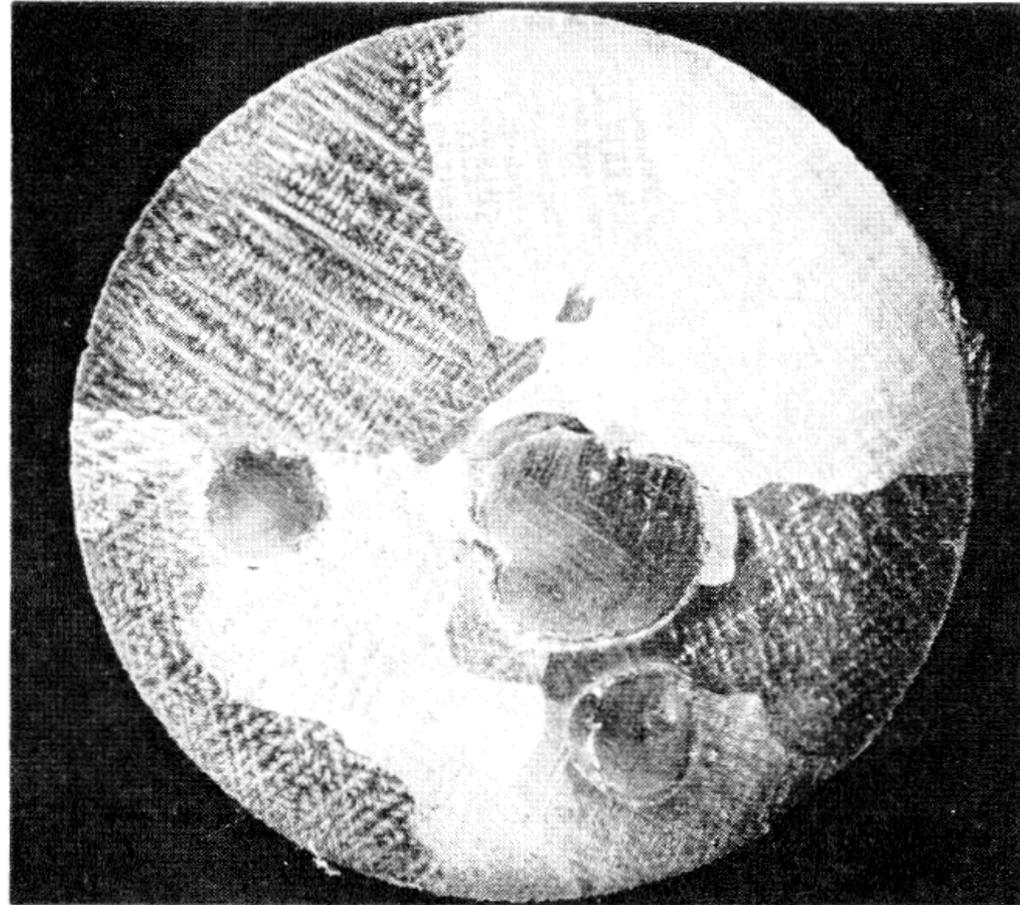


Fig. 4.23. Non-orthogonal growth of dendrite structure

* 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 grow 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.

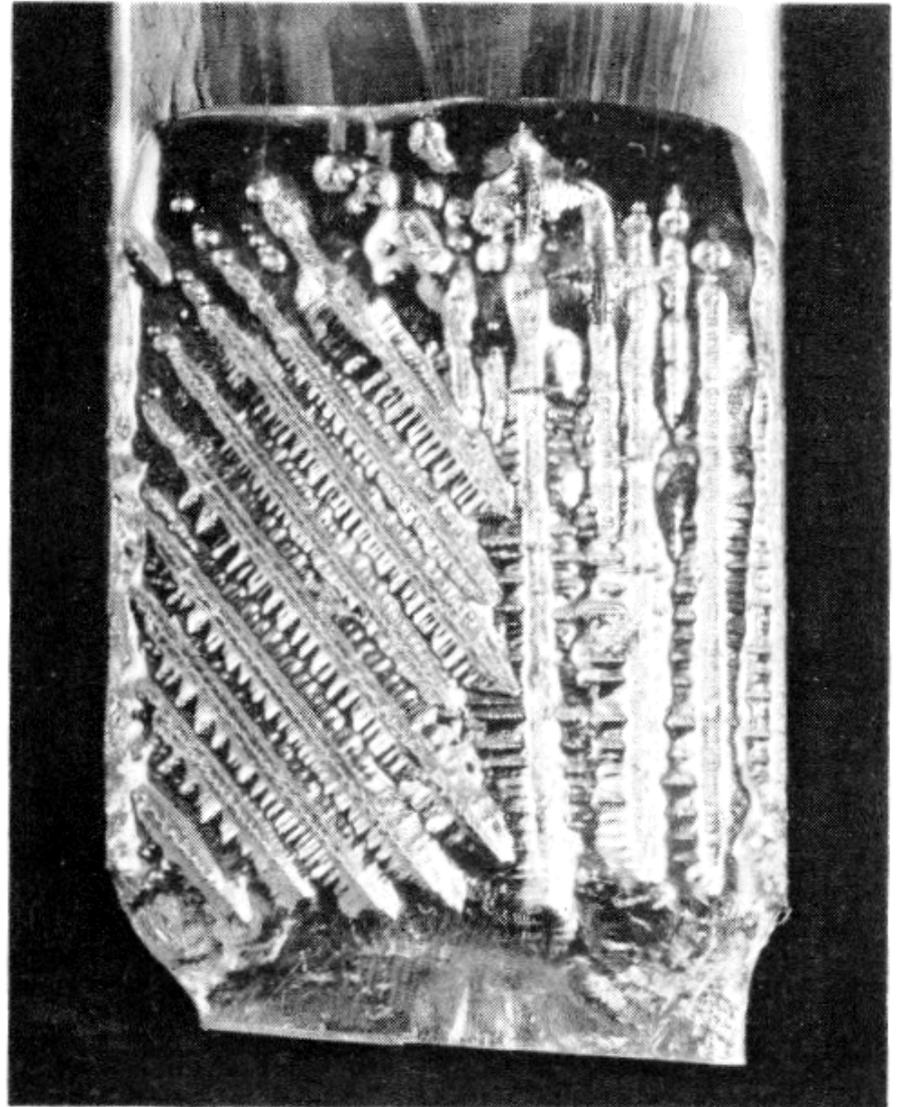


Fig. 4.24. Independence of growth direction and thermal conditions.

- * 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 $\langle 100 \rangle$ directions than in $\langle 111 \rangle$ directions.
- * Then the forward growth in a $\langle 100 \rangle$ 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.

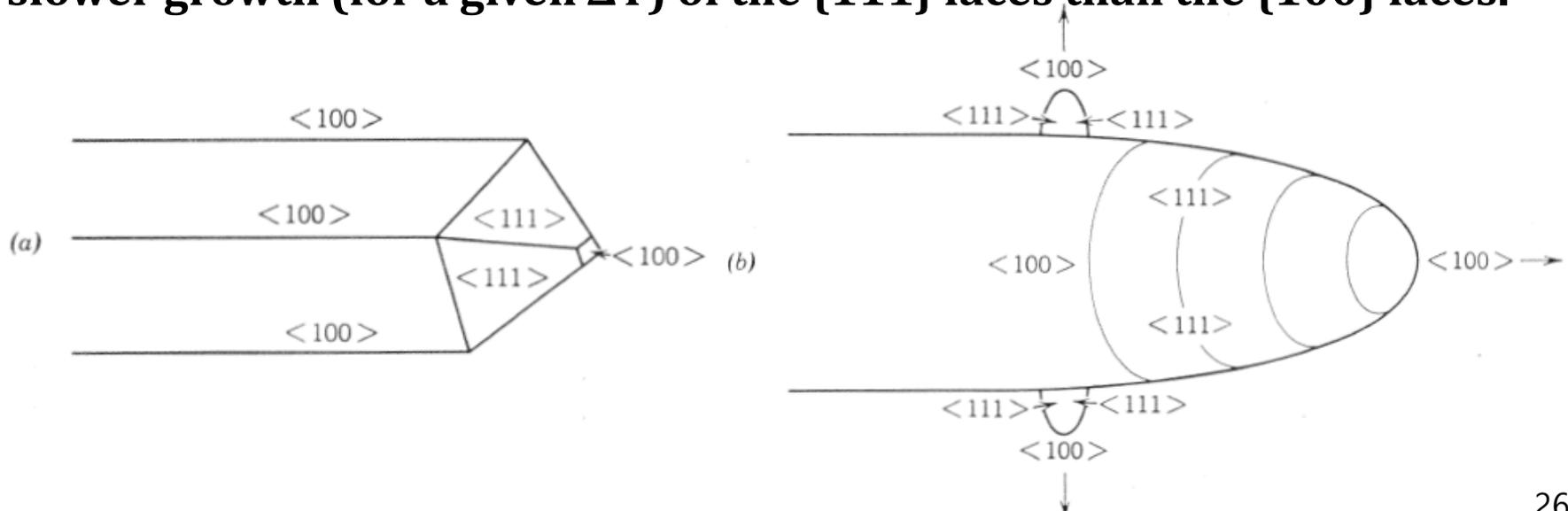


Fig. 4.25. Geometry of dendrite tip. (a) Schematic, (b) actual.

- * The transition btw $\{100\}$ and $\{111\}$ faces is through high index or non-crystallographic surfaces 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.

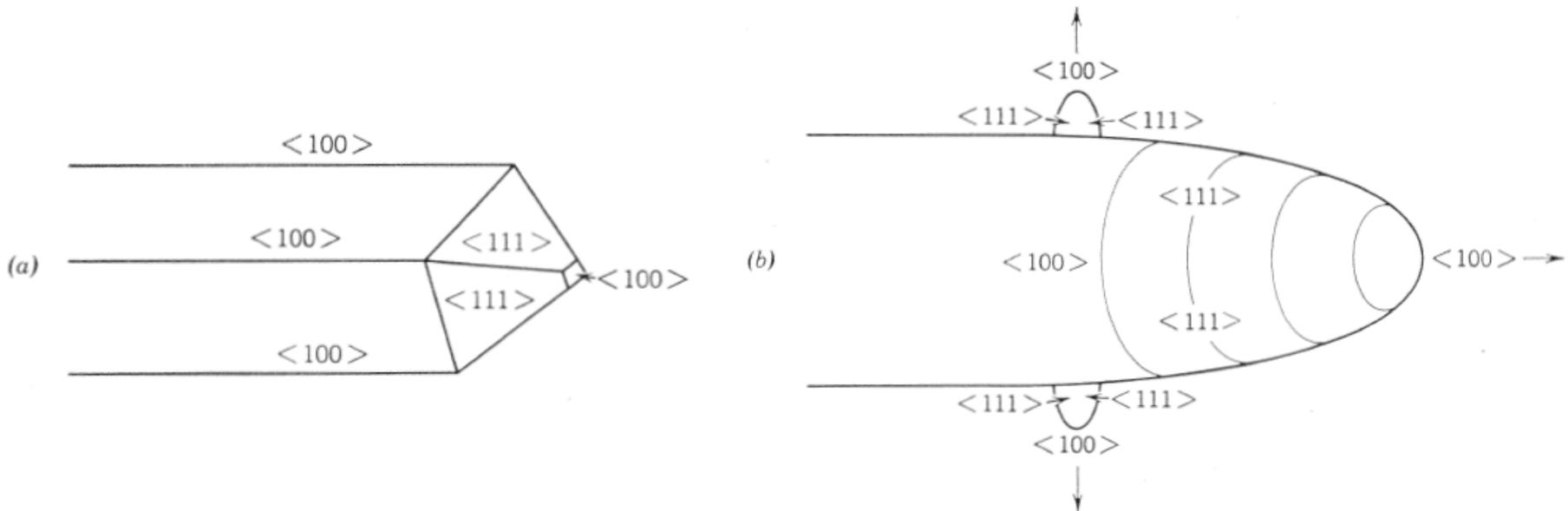


Fig. 4.25. Geometry of dendrite tip. (a) Schematic, (b) actual.

(d) Spacing and relative lengths of the branches

DIRECT OBSERVATION OF DENDRITE SHAPE

* Spacing of dendrite arms

Weinberg and Chalmer: $\Delta T \uparrow \rightarrow$ spacing of primary dendrite \uparrow

Increasing in spacing (qualitative explanation):

The region of the surface surrounding a developing instability have a smaller gradient of supercooling than regions that are undisturbed.

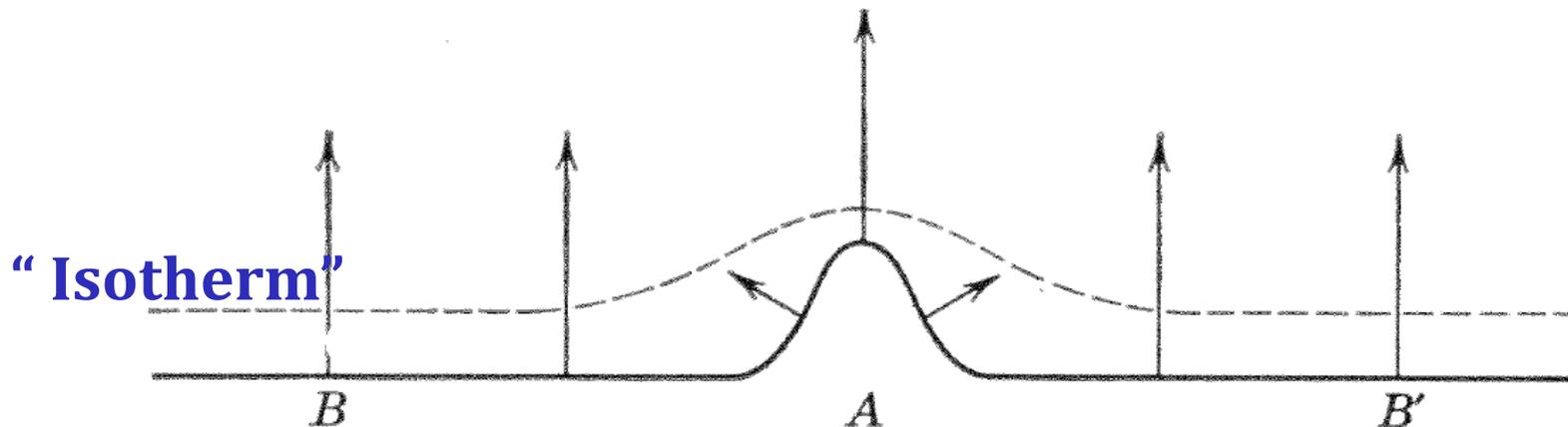


Fig. 4.26. Temperature distribution near a dendrite branch.

$\Delta T \uparrow \rightarrow$ Production rate of liquid $\uparrow \rightarrow$ AB distance \uparrow

(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 instability developed would decrease as the ΔT increased, and it would follow that the process proposed for the production of branches 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 branches.

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: $\Delta T > 175^\circ$ 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.

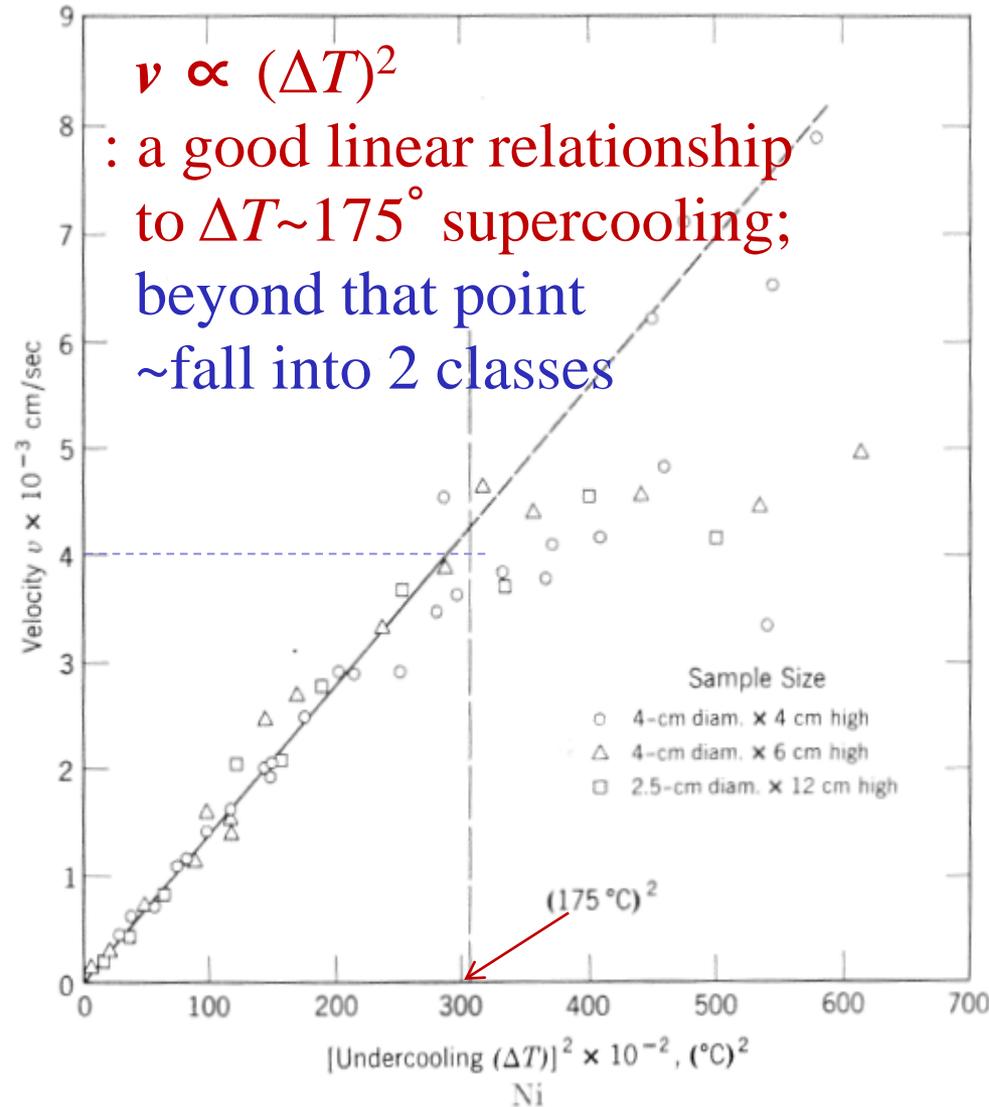


Fig. 4.20. Rate of growth of nickel in undercooled melt

$\Delta T < 175^\circ$: a few crystal, typical grain size 1.5 cm

$\Delta T > 175^\circ$: typical grain size 0.01 cm

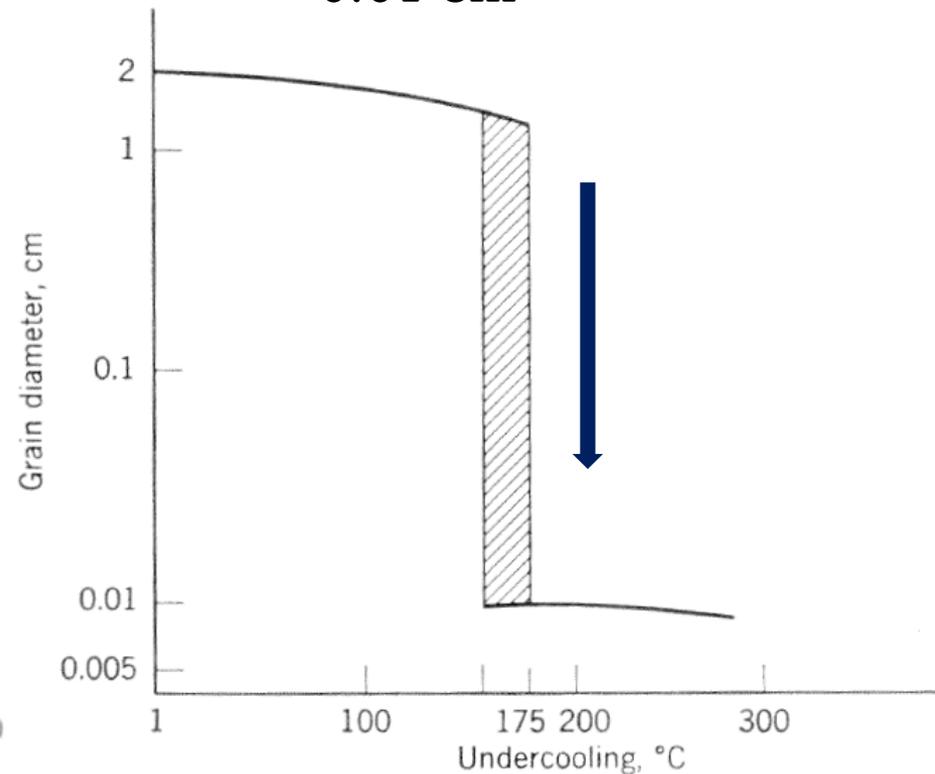


Fig. 4.27. Grain sized nickel as a function of 30 undercooling (from Ref. 26.)

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

$\Delta T < 175^\circ$: low ΔT

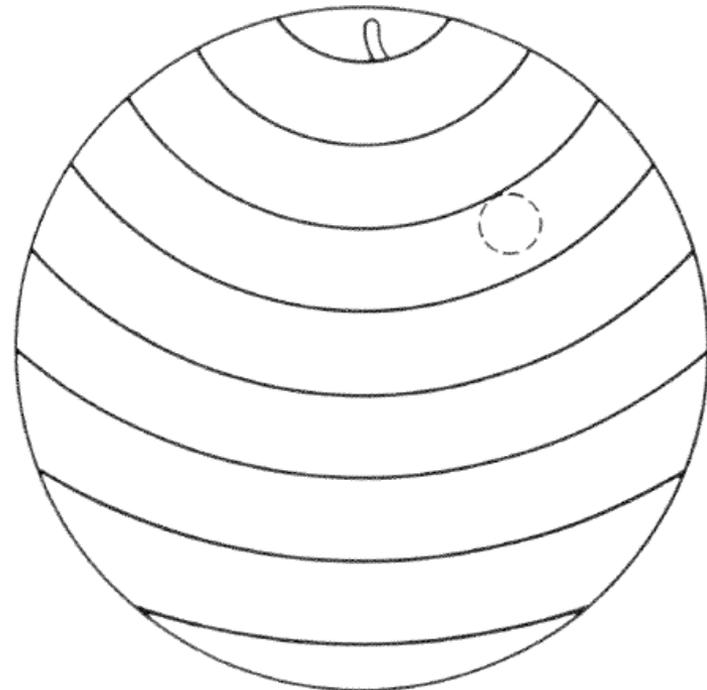
a few distinct dendrite



(a) Angular interface
 $\Delta T = 74^\circ\text{C}$

$\Delta T > 175^\circ$: high ΔT

Fine grain size
Smooth & continuous



(b) Spherical interface
 $\Delta T = 175^\circ\text{C}$

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

$\Delta T > 175^\circ\text{C}$: high ΔT

Dendritic growth of existing crystals

→ Interrupted by the nucleation of new crystals

→ again interrupted by the formation of more crystals

$\Delta T < 175^\circ\text{C}$: low ΔT

Crystal size $\sim t^{1/2}$

→ 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 ($\Delta T \sim 175^\circ\text{C}$) when the cavitation pressure reached.

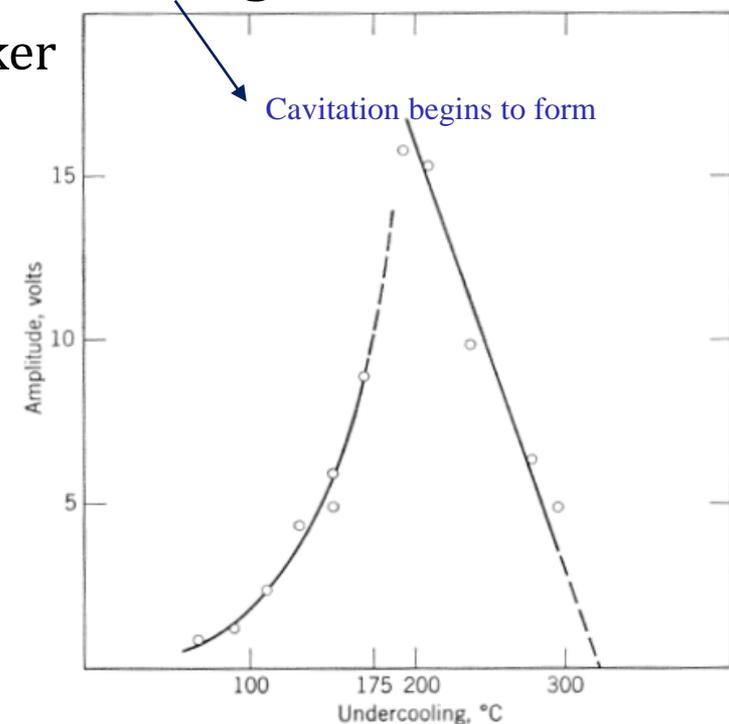
As the crystal grows, the negative pressure passes through max. value.

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.

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



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”

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



$$S \approx C \Delta T / L.$$

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

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

b) Non-steady state theory

Growth vs. branching of dendrite : periodicity of process

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

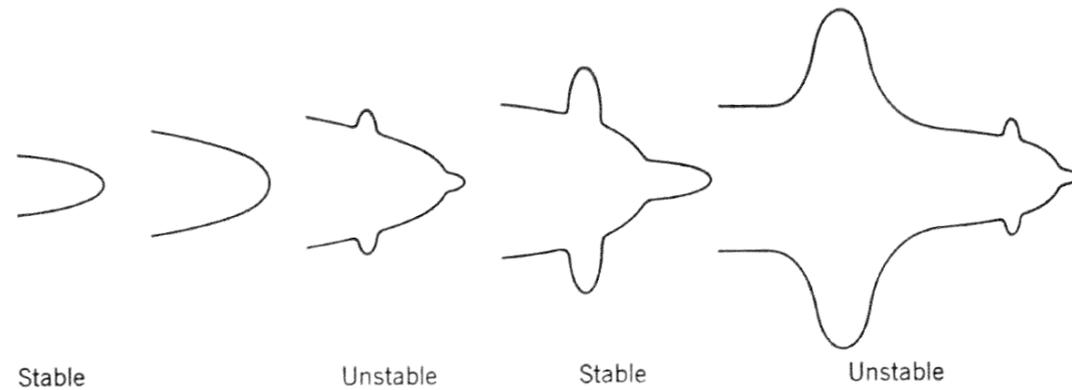


Fig. 4.14. Branching of dendrites.

* EXPERIMENTAL OBSERVATION OF RATE OF DENDRITIC GROWTH

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

(2) lead dendrite with diffuse interface grew much faster than that with smooth interface

(3) R data: Scattering

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

b) 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 interference by the overlapping of their thermal fields.

(4) $v \propto (\Delta T)^2$: a good linear relationship to $\Delta T \sim 175^\circ$ 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 \propto temp gradient & radius)

(C) Direction of dendrite growth

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.

Table 4.1. Direction of Dendritic Growth

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

- 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.
- 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. → Independence of growth direction and thermal conditions.

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

(d) Spacing and relative lengths of the branches

DIRECT OBSERVATION OF DENDRITE SHAPE

* Spacing of dendrite arms

Weinberg and Chalmer: $\Delta T \uparrow \rightarrow$ spacing of primary dendrite \uparrow

Increasing in spacing (qualitative explanation):

The region of the surface surrounding a developing instability have a smaller gradient of supercooling than regions that are undisturbed.

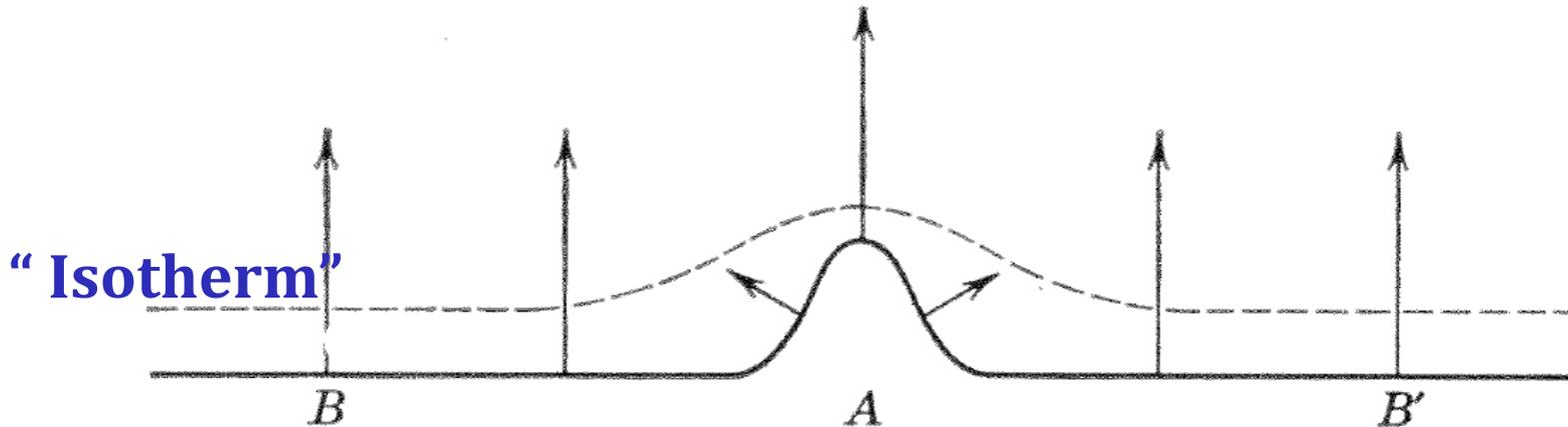


Fig. 4.26. Temperature distribution near a dendrite branch.

$\Delta T \uparrow \rightarrow$ Production rate of liquid $\uparrow \rightarrow$ AB distance \uparrow
(the gradient is insufficient to allow arms to develop).

Solidification: Liquid \longrightarrow Solid

- Undercooling ΔT
- Interfacial energy $\gamma_{SL} / S(\theta)$ wetting angle

1) Pure Metals: Nucleation and Growth

a) homogeneous Nucleation or Heterogeneous Nucleation

b) Growth of solid

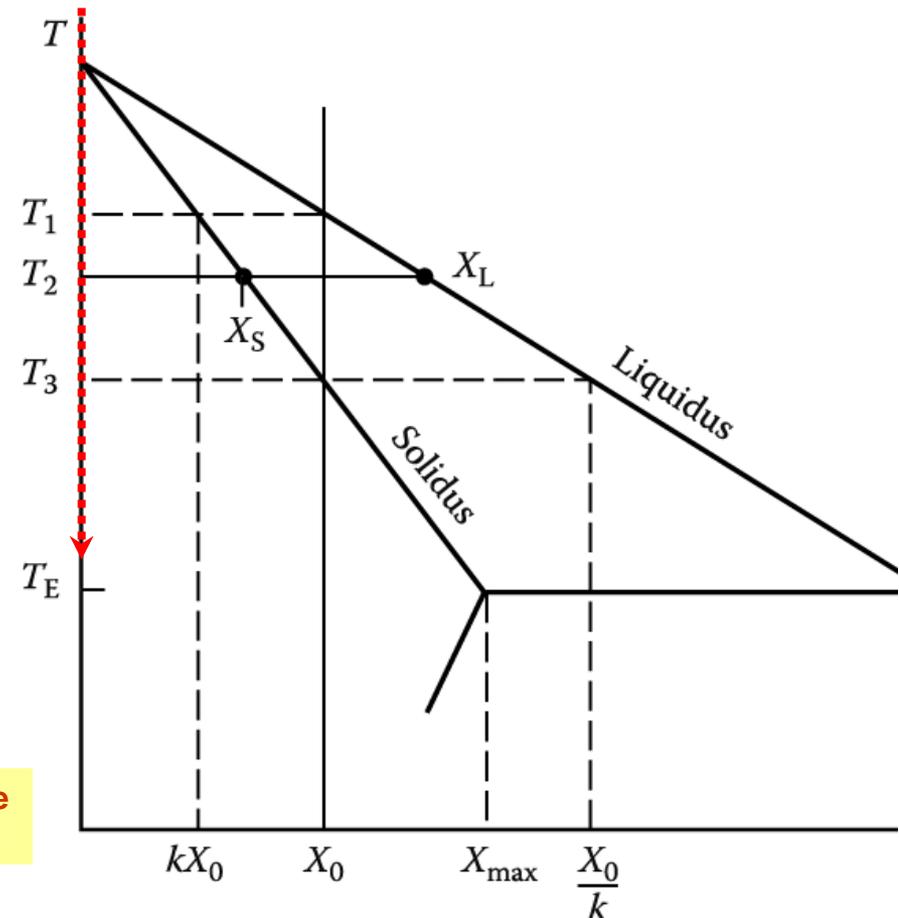
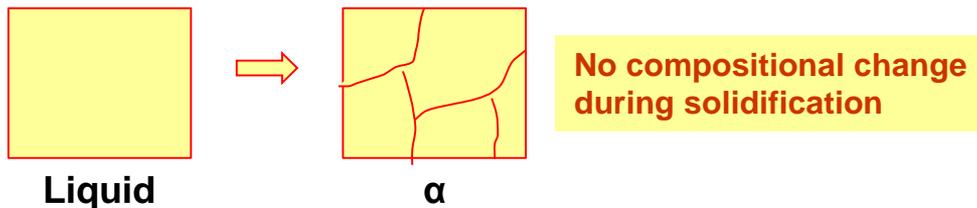
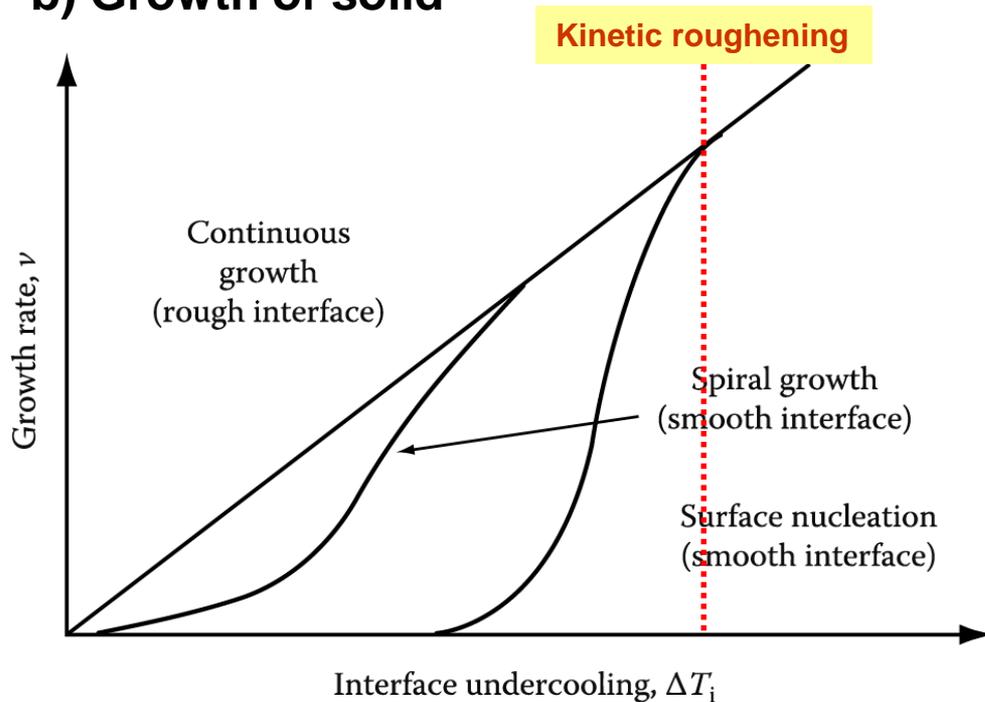


Fig. 4.19 A hypothetical phase diagram.

“Alloy solidification”

1. Solidification of single-phase alloys

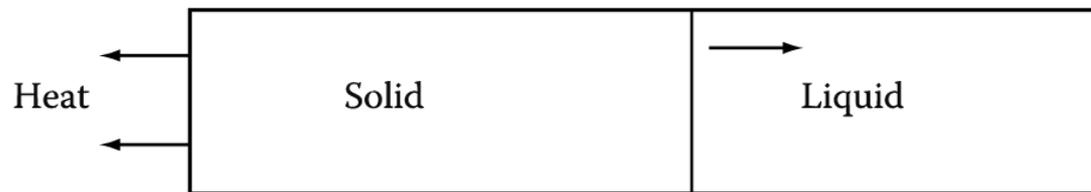
- Three limiting cases

1) Equilibrium Solidification: perfect mixing in solid and liquid

2) No Diffusion on Solid, Diffusional Mixing in the Liquid

3) No Diffusion in Solid, Perfect Mixing in Liquid

- Planar S/L interface → unidirectional solidification



x → - Superheated liquid

- Cellular and Dendritic Solidification

- Supercooled liquid

Chapter 5. Redistribution of solute during solidification

5.2 The Distribution Coefficient

Distribution coefficient or partition coefficient, k

a) **Equilibrium distribution coefficient** $k_0 = C_S/C_L$ Characteristic of the system

- Not necessarily a constant for a given system
(\because liquidus & solidus line may not be so related as to maintain a constant ratio)
- Independent of the speed of the motion of the interface

b) **Effective distribution coefficient** $k_E = C_S/C_0$ Depends of the conditions under which solidification takes place

C_S is formed at some instant by solidification of a liquid of average concentration C_0

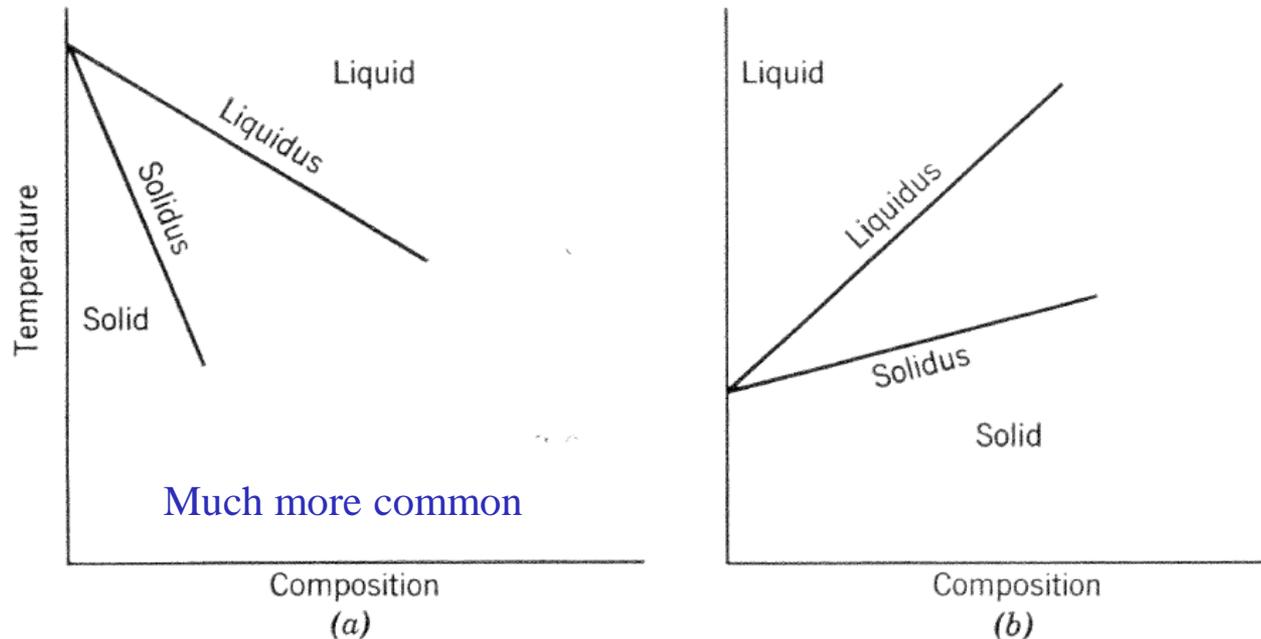


Fig. 5.1. Solidus-liquidus relationships for dilute binary alloys.

5.3 Rejection of solute

At solid-liquid interface

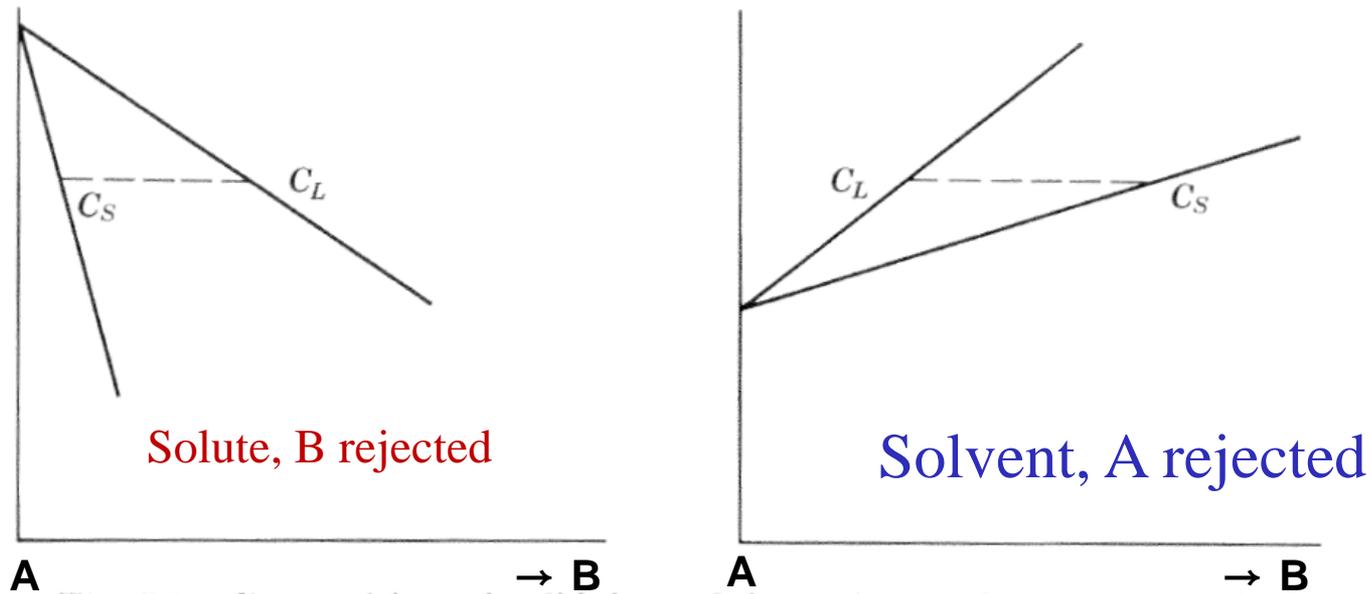


Fig. 5.3. Composition of solid formed from liquid of composition C_L .

* Both heat flow and solute diffusion are uniaxial
 → constant speed of interface

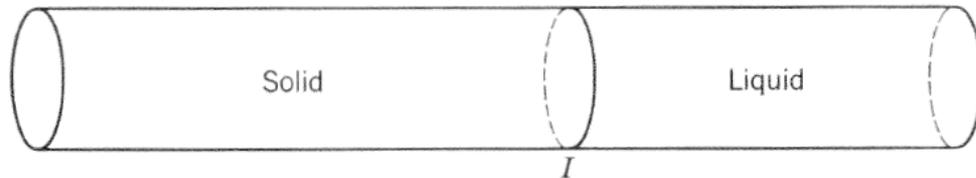


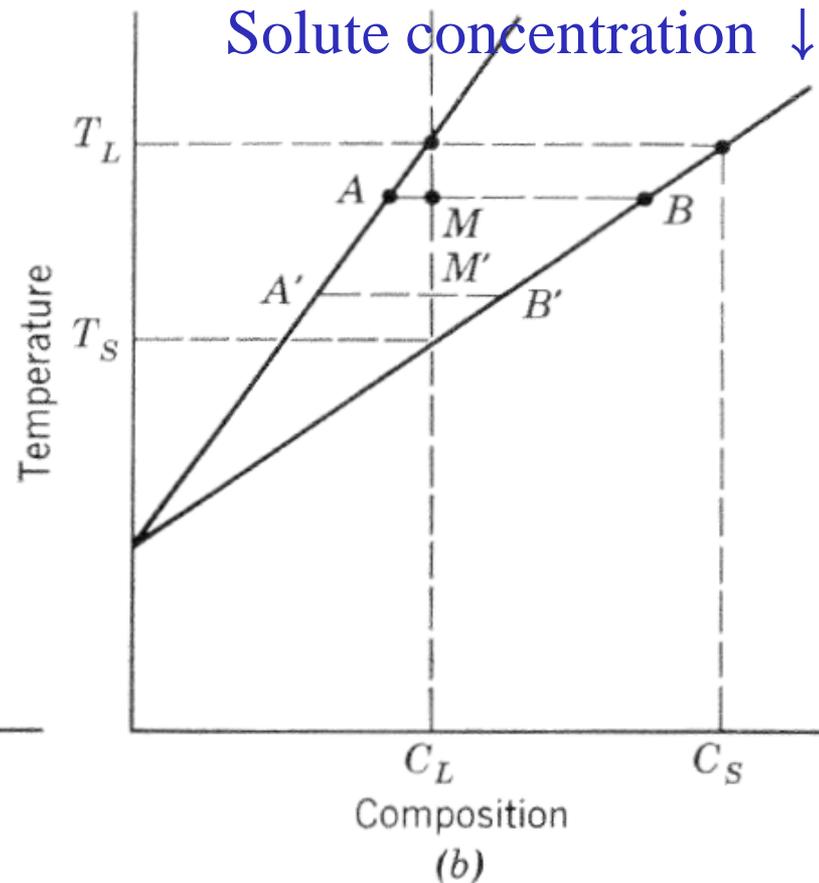
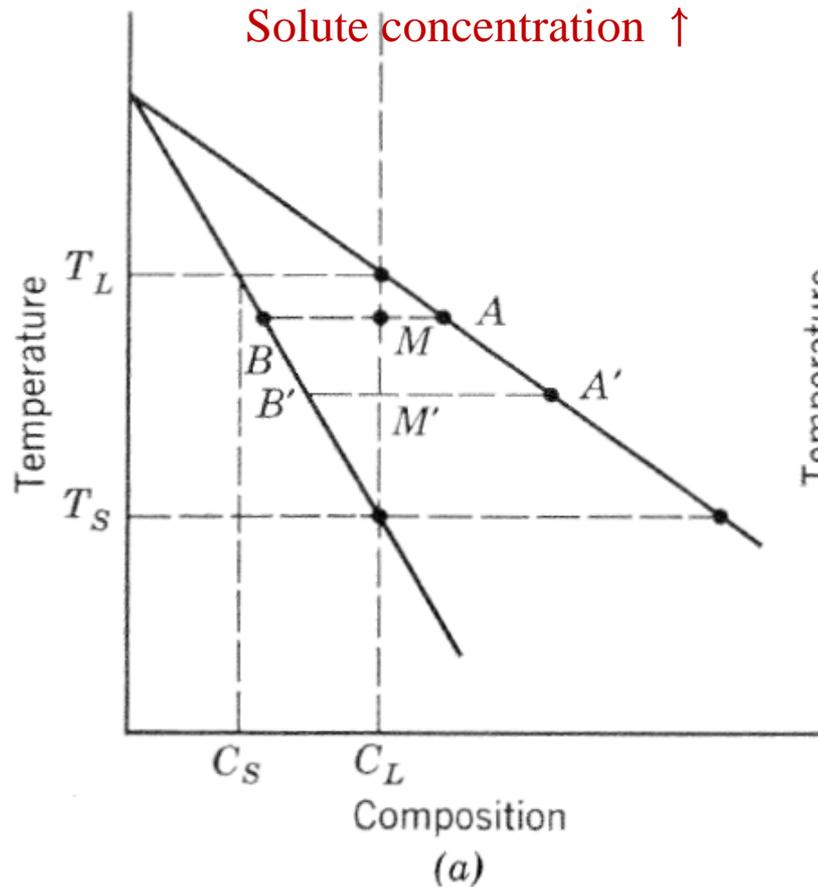
Fig. 5.4. Geometry of uniaxial solidification.

Assumption:

- (a) all times completely mixed with the whole of remaining liquid.
- (b) Transport is by diffusion only.
- (c) Motion of solute, by diffusion, in the solid

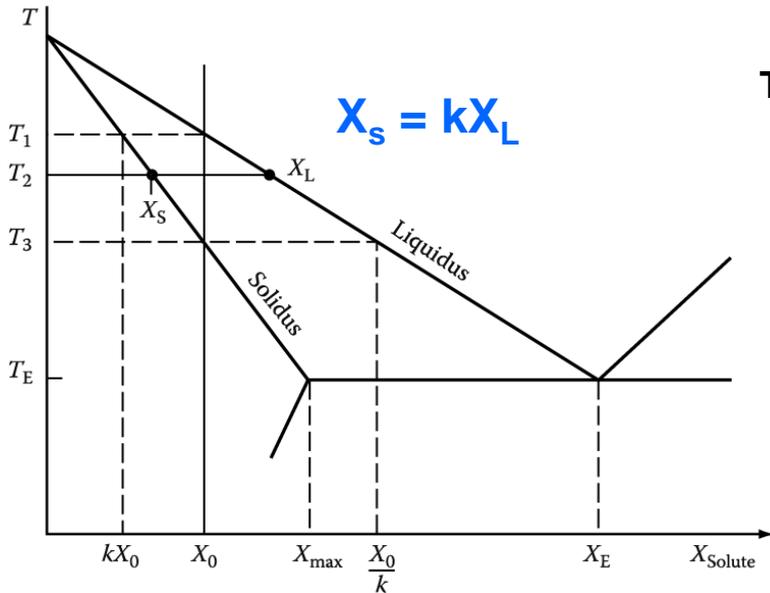
1) Equilibrium maintained at all times: perfect mixing in solid and liquid

When solidification start \rightarrow liquidus temp \downarrow



- a) Total amount of solvent and solute remain unchanged.
- b) The relative amount of solid and liquid are always given by the ratio AM/BM .

1) Equilibrium Solidification : perfect mixing in solid and liquid

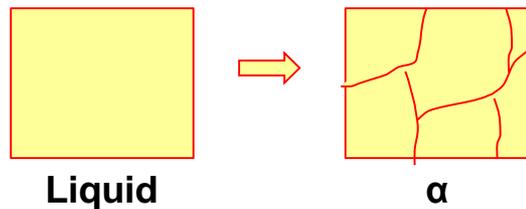


Conservation of solute requires the two shaded areas to be equal.

* Equilibrium solute concentration

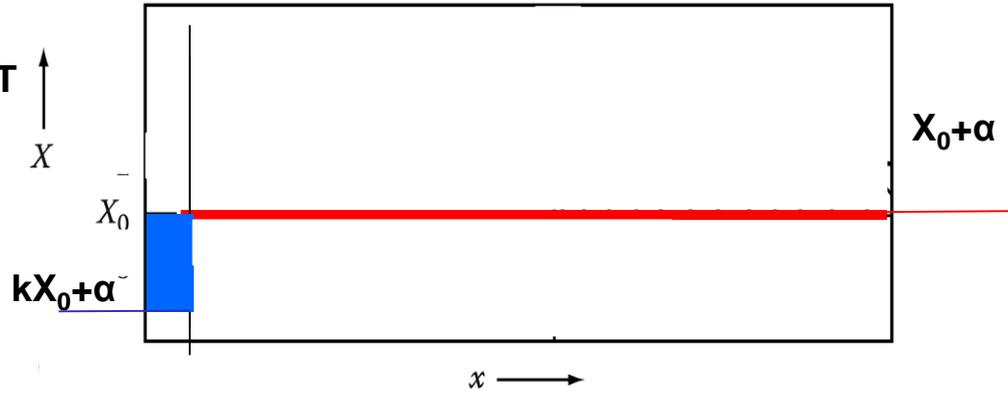
$$kX_0 \leq X_s \leq X_0$$

$$X_0 \leq X_L \leq X_0/k < X_E$$

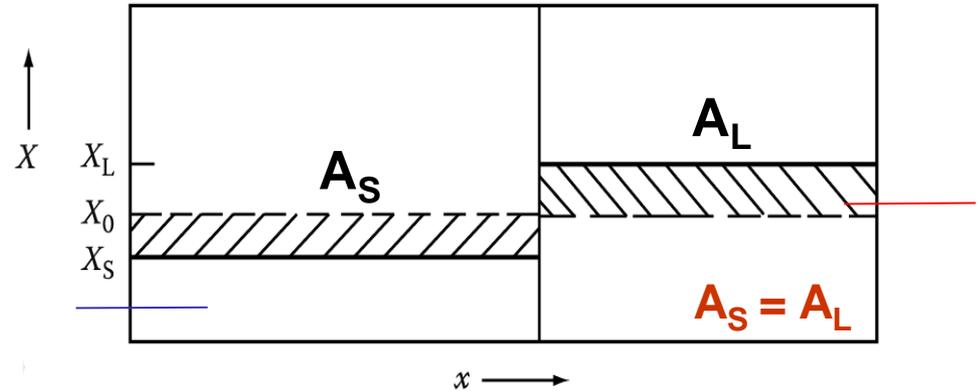


Compositional change during solidification

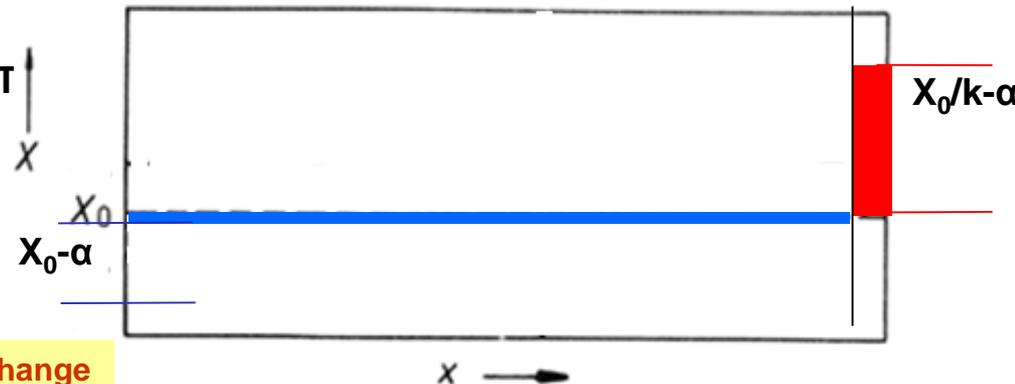
$T_1 - \Delta T$



T_2



$T_3 + \Delta T$



1) Equilibrium Solidification : perfect mixing in solid and liquid

a) Solid is at all times in equilibrium with the liquid →

“diffusion in Solid ~ fast enough” → **no concentration gradient**

* The assumption demands that

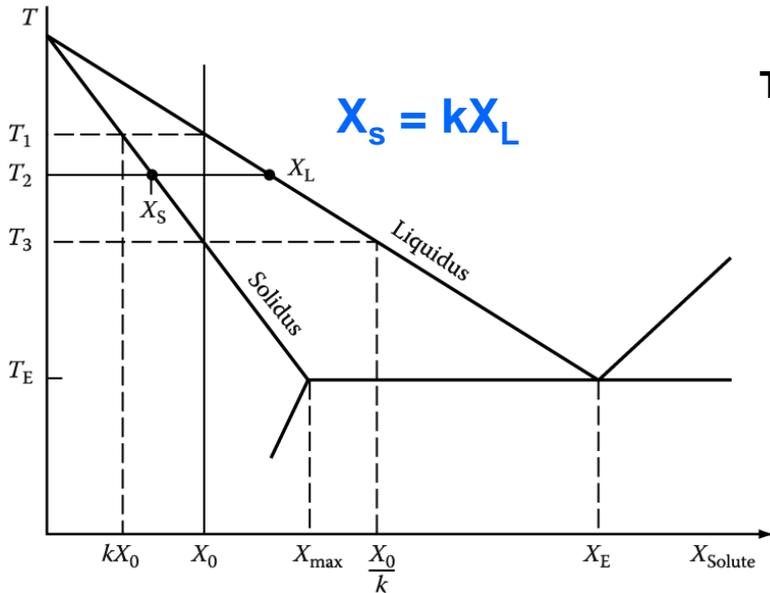
① the rate of advance of the interface is slow compared with the diffusion rate of the relevant solute in the solid

② diffusion distance (total distance through which the interface moves) is small.
(for example, geological process, the time scale is extremely long by human or industrial standards)

b) Among metallurgical processes, the largest effect of diffusion during solidification is probably to be found in the case of carbon and nitrogen in steel, since these interstitial solutes have very much higher diffusion coefficients than substitutional solutes.

c) It should also be remembered that a significant amount of diffusion can also take place after solidification while the material is cooling down. → page 178

1) Equilibrium Solidification : perfect mixing in solid and liquid

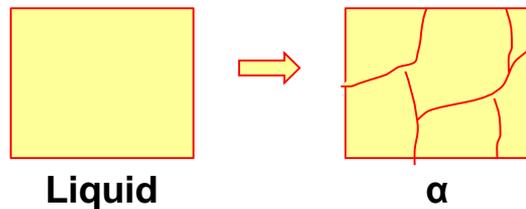


Conservation of solute requires the two shaded areas to be equal.

* Equilibrium solute concentration

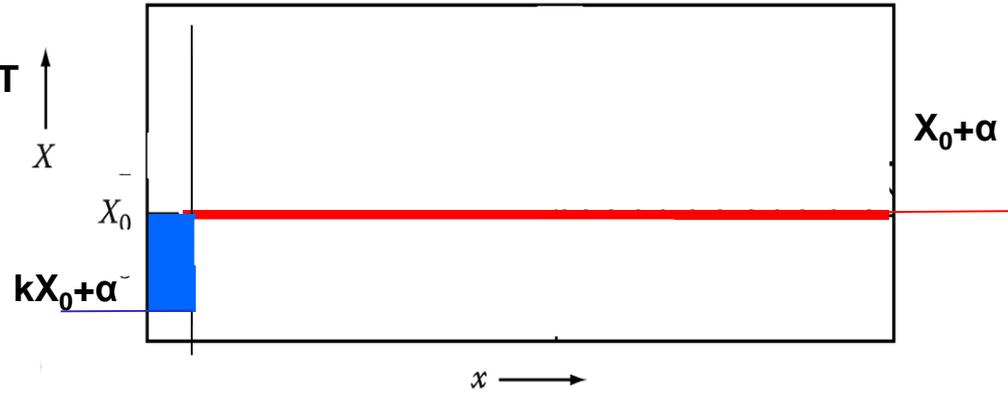
$$kX_0 \leq X_s \leq X_0$$

$$X_0 \leq X_L \leq X_0/k < X_E$$

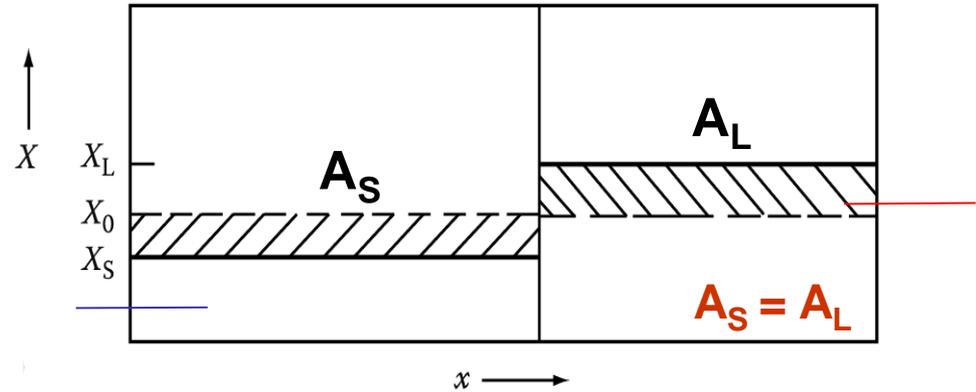


Compositional change during solidification

$T_1 - \Delta T$



T_2



$T_3 + \Delta T$

