CHULA ΣNGINEERING
Foundation toward Innovation

Solidification of Metal

Introduction to Materials

Science and Engineering

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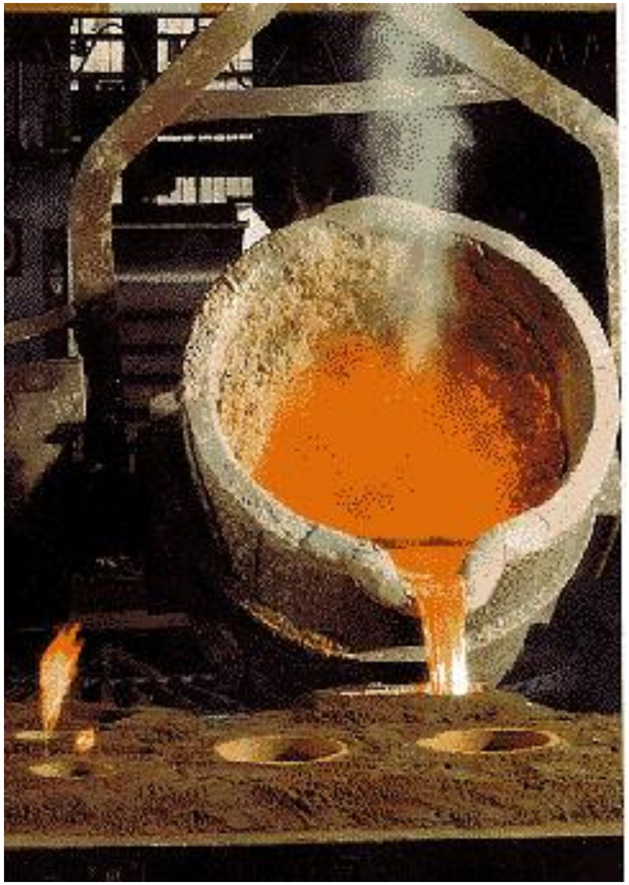
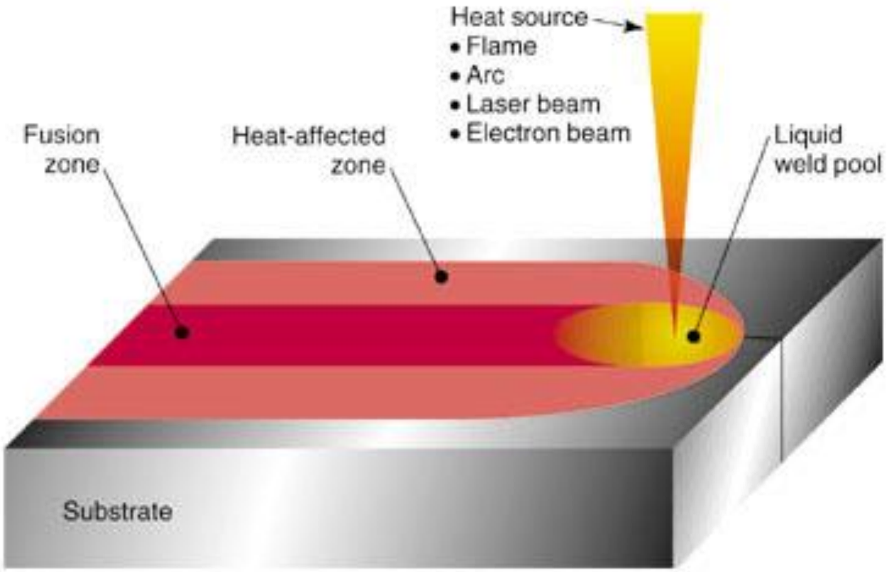
Processes involving solidification



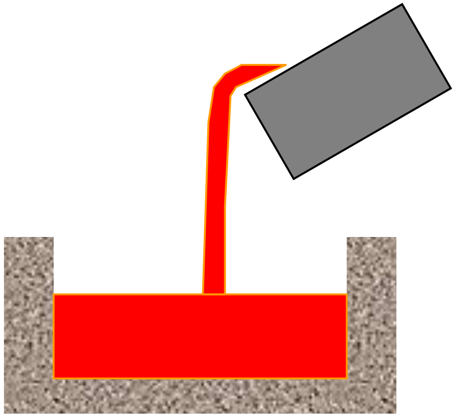
Metal Casting
(fully solidification)



Welding
(Partial Solidification)

Casting is

- Liquid metal is poured into carefully designed mould cavity and solidifies into a desired shape under controlled conditions
- The first step in all manufacturing processes involving metal



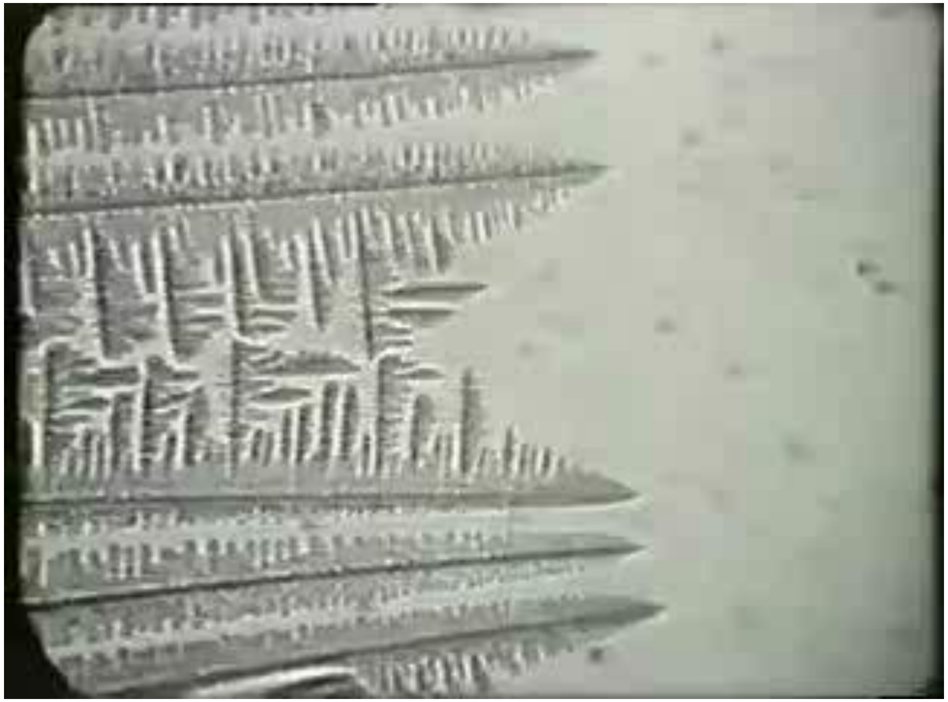
Preceded by:

- liquid metal extraction
- refining and alloying processes

Followed by:

- Heat treatment (to alter properties)
- Shape change (rolling, forging, drawing, pressing, machining, etc.)
- Finishing (surface control)

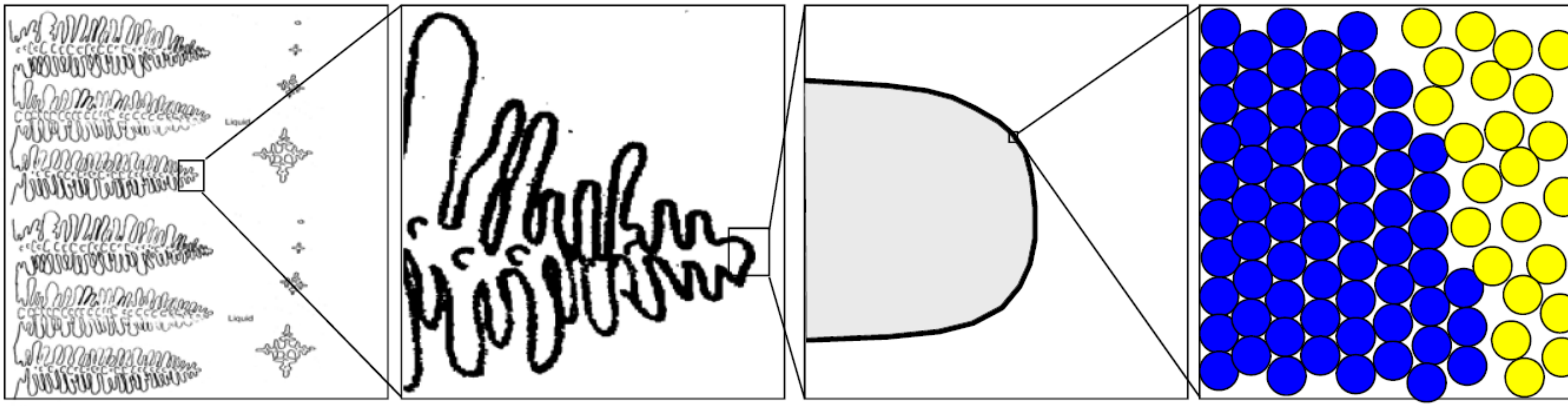
Solidification: Dendrite growth



Columnar dendrites

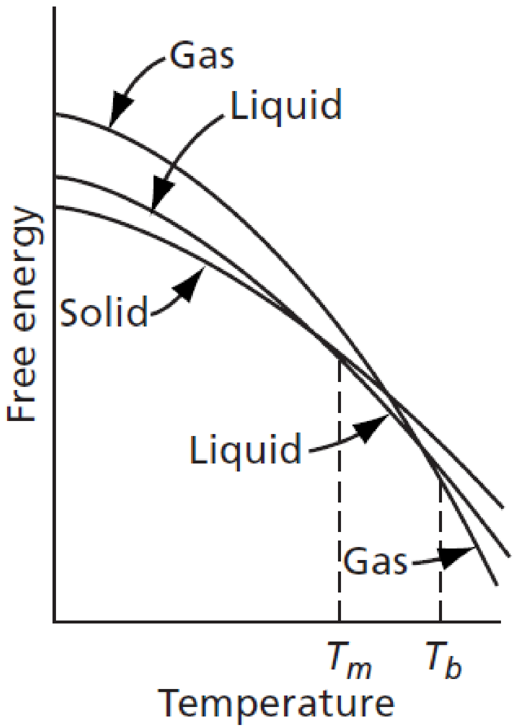
Equiaxed dendrites

Solidification phenomena: multi-scale

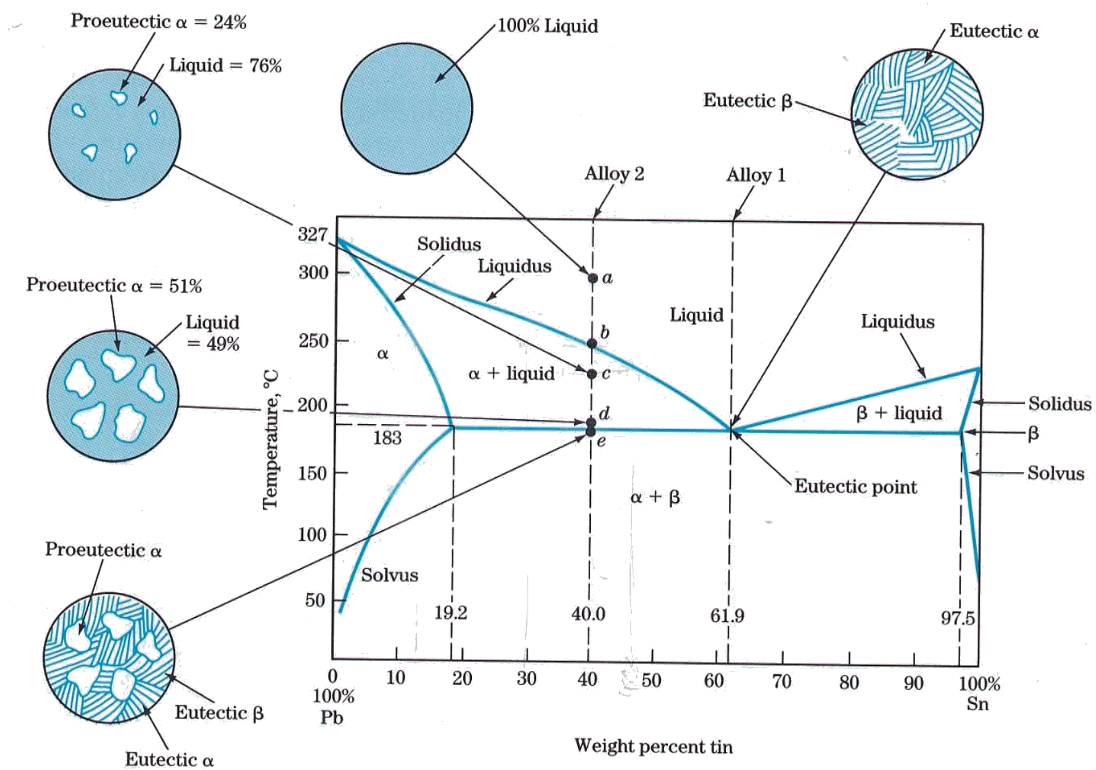


Macroscopic	Microscopic	Interface	Atomic
10^{-2} m	10^{-4} m	10^{-5} m	10^{-8} m
Transport phenomena – mass, momentum, heat & species, latent heat evolution, grain structure, shrinkage	Columnar & equiaxed cells and dendrites, eutectics, coarsening, species transfer, front behavior, spacings	Interface instabilities, capillarity, undercooling, local equilibrium	Nucleation, interface structure (faceted / non-faceted), atomic attachment kinetics, nanoscale quantum effects

Free-energy curve and Phase Diagram



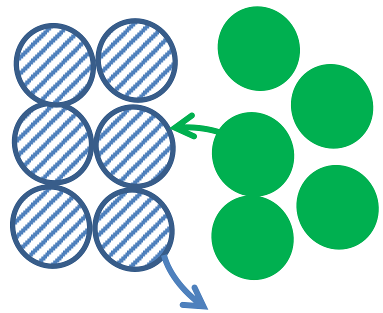
Free-energy curves for the phases in a one-component system



Binary Phase Diagram

Crystal growth from liquid phase

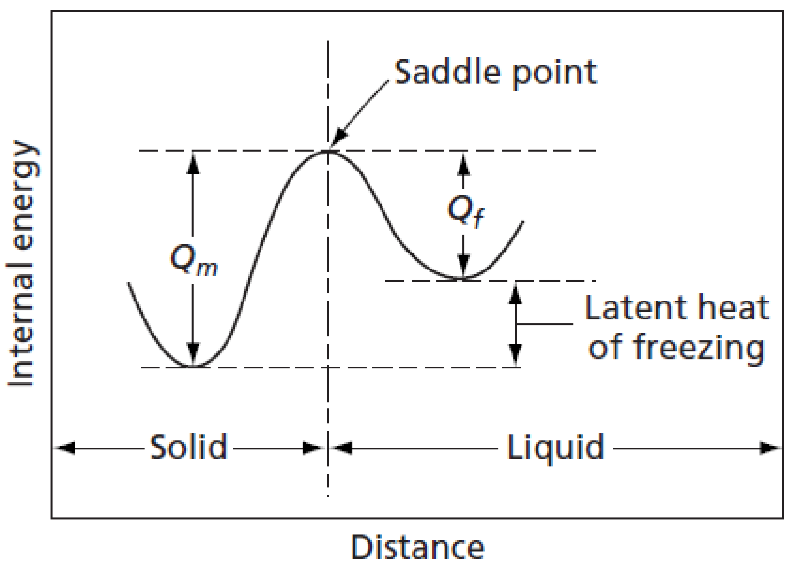
Those that travel in the opposite direction determine a rate of detachment



Those atoms that leave the liquid and join the solid determine a rate of attachment

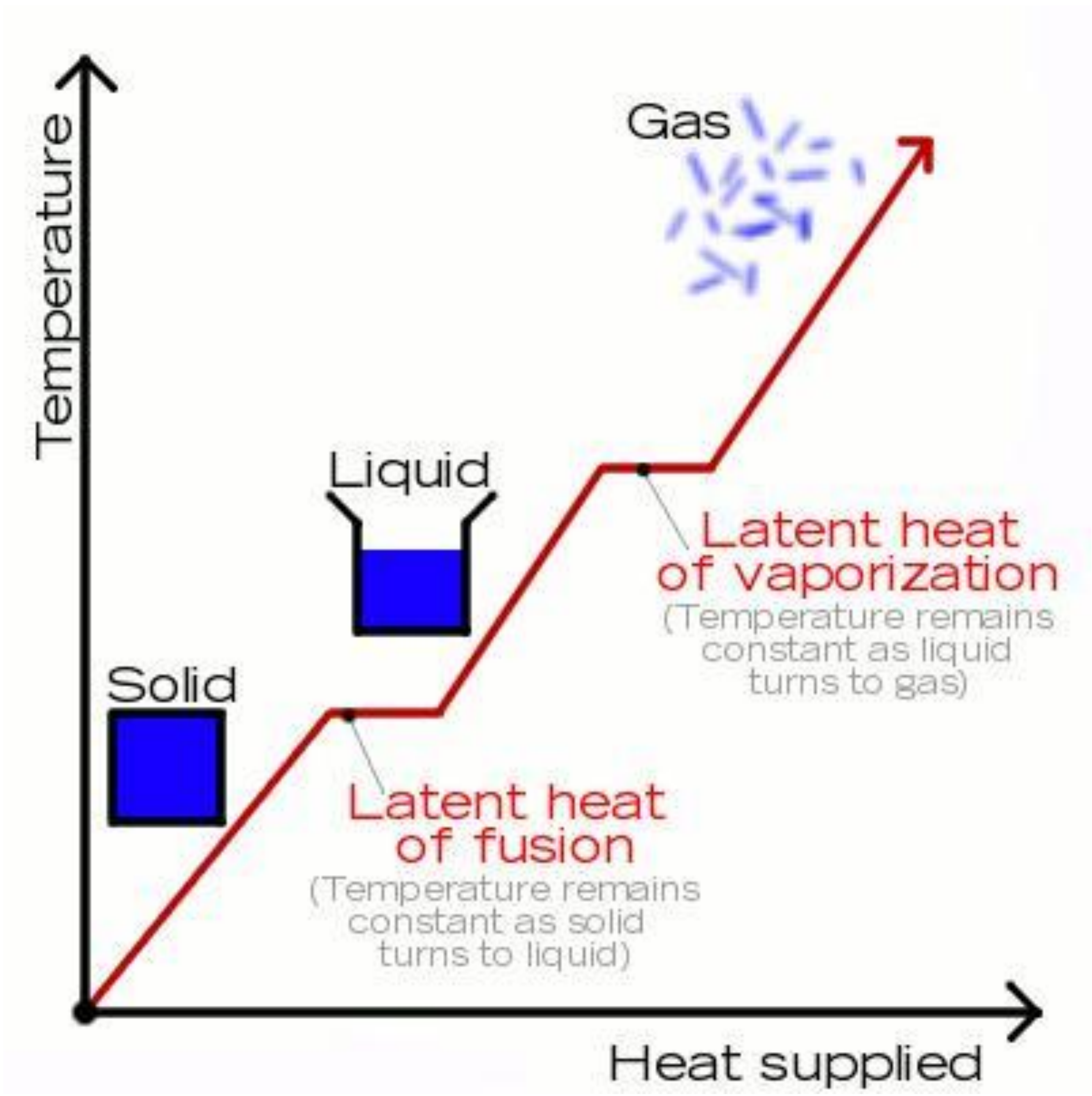
$$R_m = R_{m_0} e^{-Q_m/RT}$$

$$R_f = R_{f_0} e^{-Q_f/RT}$$



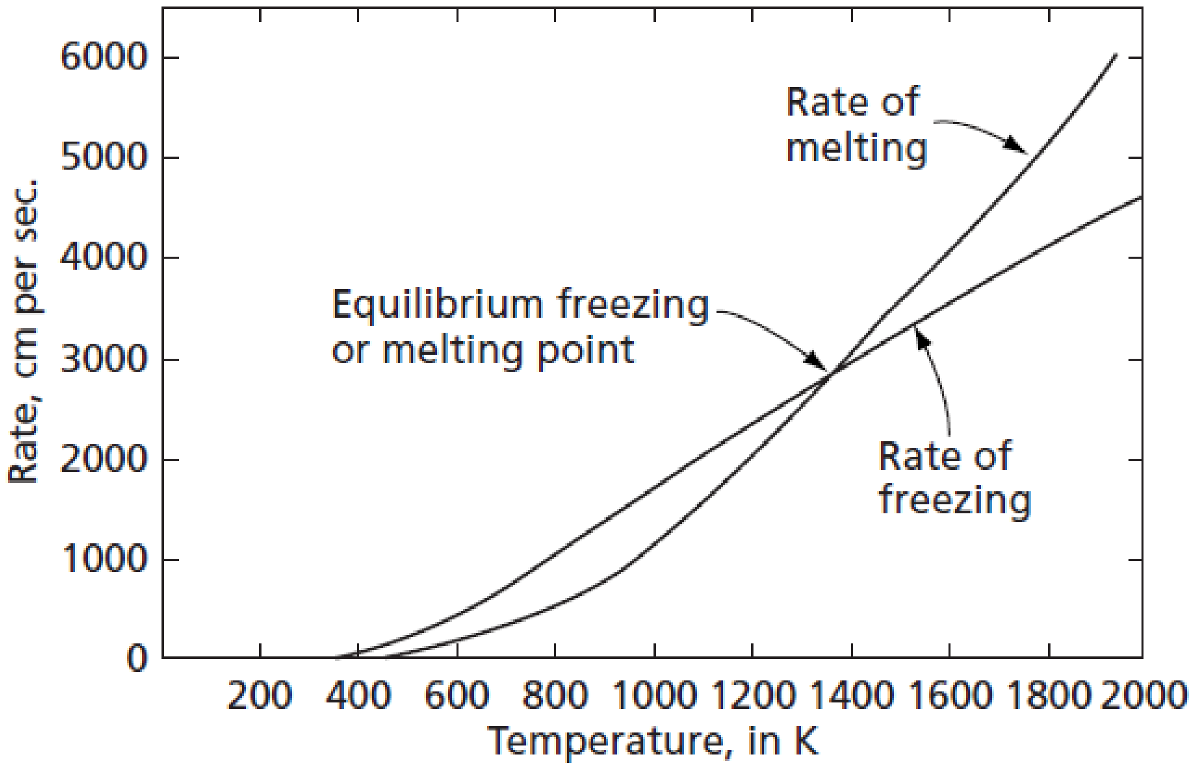
An atom in the solid possesses a lower energy than one in the liquid, but it should be noted that it also possesses a lower entropy

Latent heat



Temperature
Gas
Liquid
Solid
Latent heat
of vaporization
(Temperature remains
constant as liquid
turns to gas)
Latent heat
of fusion
(Temperature remains
constant as solid
turns to liquid)
Heat supplied

Rates of freezing and melting for copper



The curves for the freezing rate and the melting rate as functions of temperature

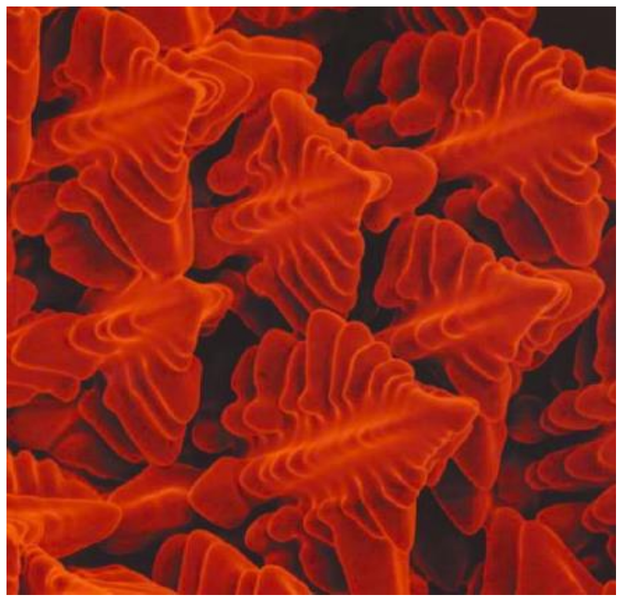
The difference in the individual rates determines the actual rate with which the interface moves

The observed growth rate, or melting rate, increases as the temperature deviates from the equilibrium freezing point

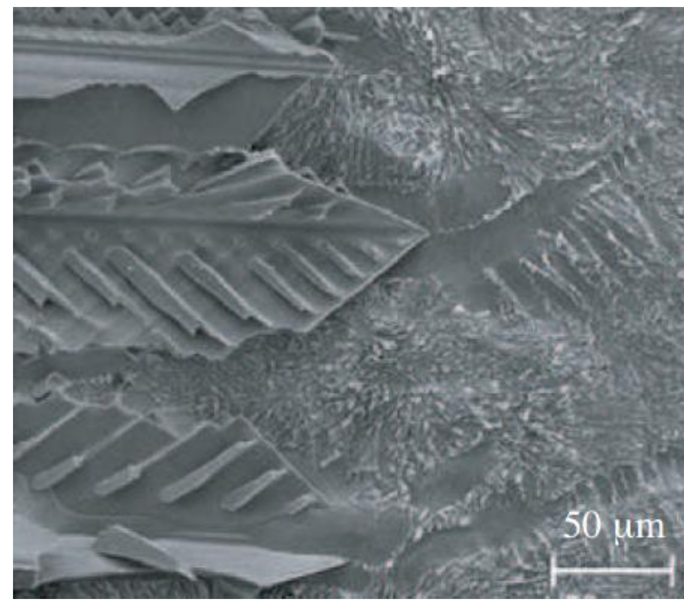
Growth of Solid

- The preference of growth is derived from **anisotropy**:
  - Kinetics of atom attachment to the interface
  - Surface energy of solid-liquid interface

Succinonitrile dendrite



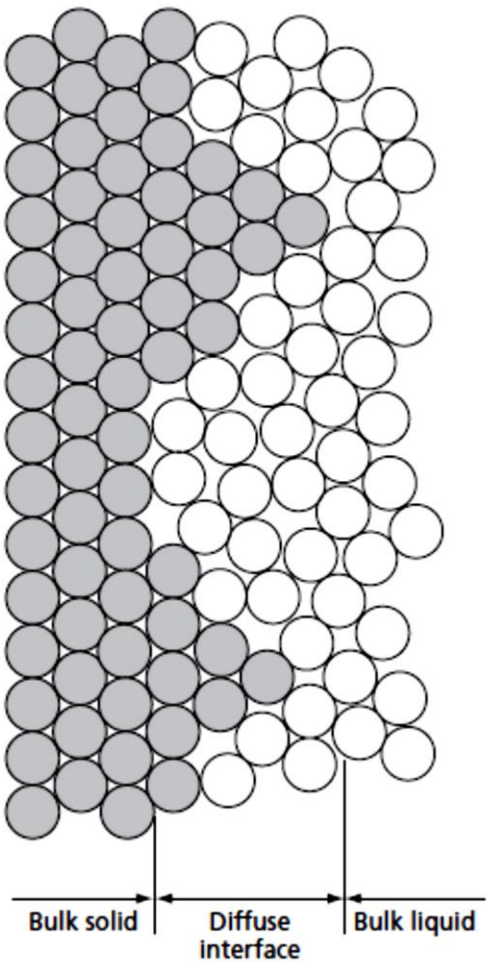
Ni dendrites in superalloys



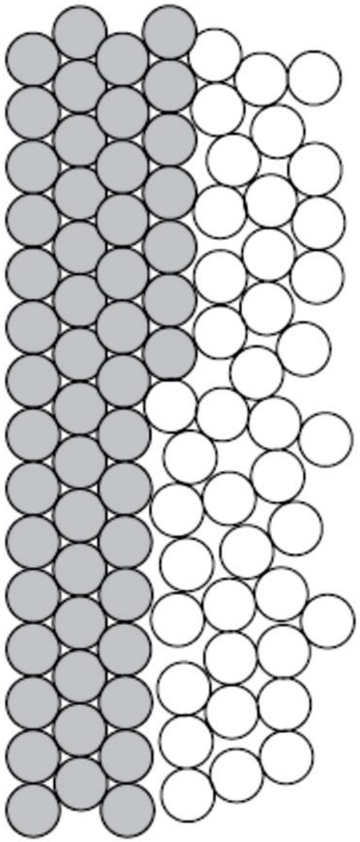
Faceted Si dendrite in Si-Al alloy

Nature of solid-liquid interface

Diffuse interface



Smooth interface



Atomically Diffuse interface

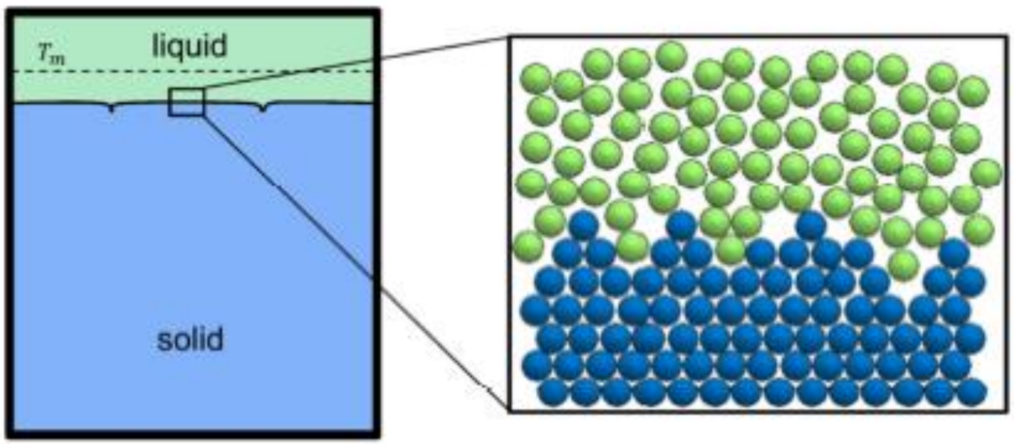
- Structure and bonding between the two phases is similar
- Interface has a very high accommodation factor for the liquid atoms
- addition of atoms continuously at every atomic site

Atomically Smooth interface

- Difference in structure and bonding between the two phases is great
- limited by attachment

Solid-Liquid Interface

Non-facetted Structure



$$\Delta S_f{}^m = S_L{}^m - S_S{}^m < 2R$$

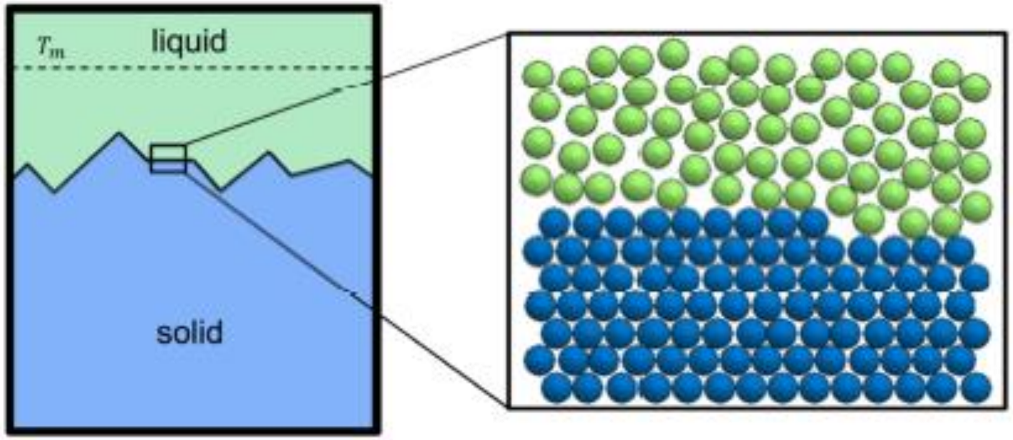
R is gas constant

e.g. metals

Jackson' α factor

$$\alpha = \frac{\Delta S_f{}^m}{R} = \frac{L_f}{T_m R} < 2$$

Facetted Structure



$$\Delta S_f{}^m = S_L{}^m - S_S{}^m > 2R$$

$$\alpha > 2$$

e.g. intermetallics and semi-conductors

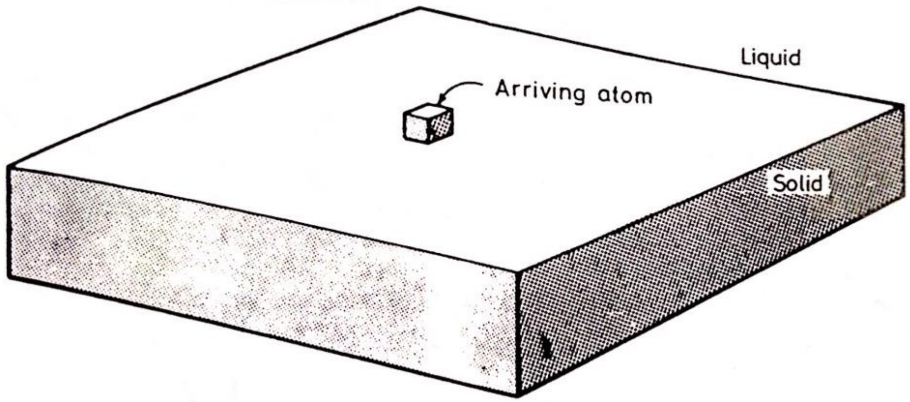
Continuous growth VS Lateral growth

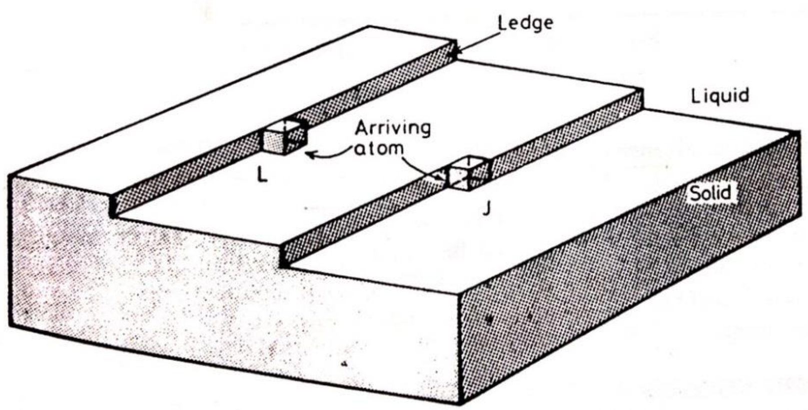
Continuous growth

- Atomically diffuse interface: atoms can be easily received at any site on solid structure
- Solidification of metals is usually diffusion controlled process
  - Pure metals - heat conduction (diffusion)
  - Alloys - solute diffusion

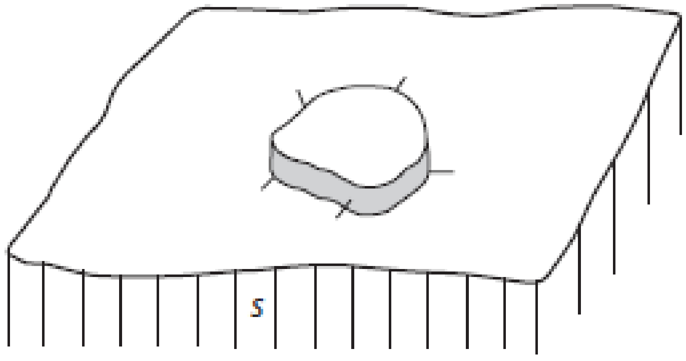
Lateral growth

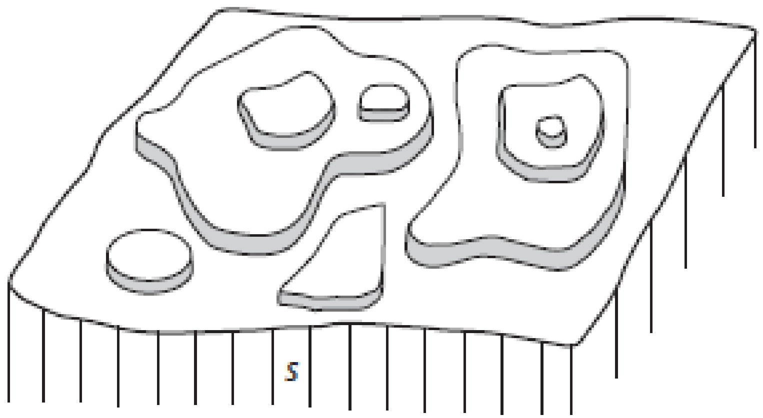
- Atomically smooth interface : very high free energy is anticipated to position one atom/molecule at the solid surface
- Atoms are usually attached to solid at steps and may sometimes prefer defects

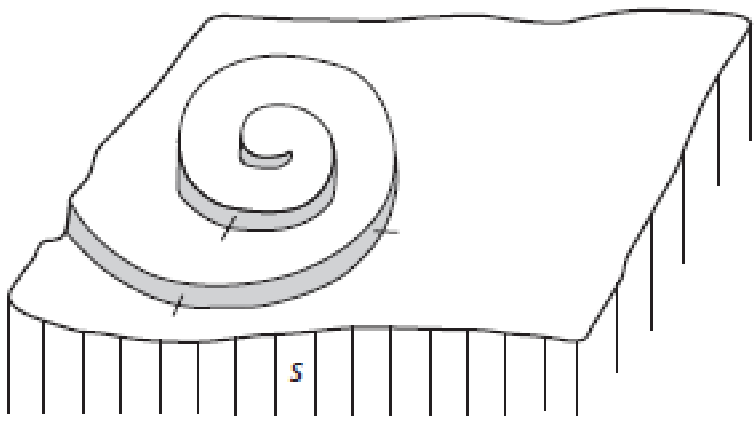




Lateral growth mechanisms







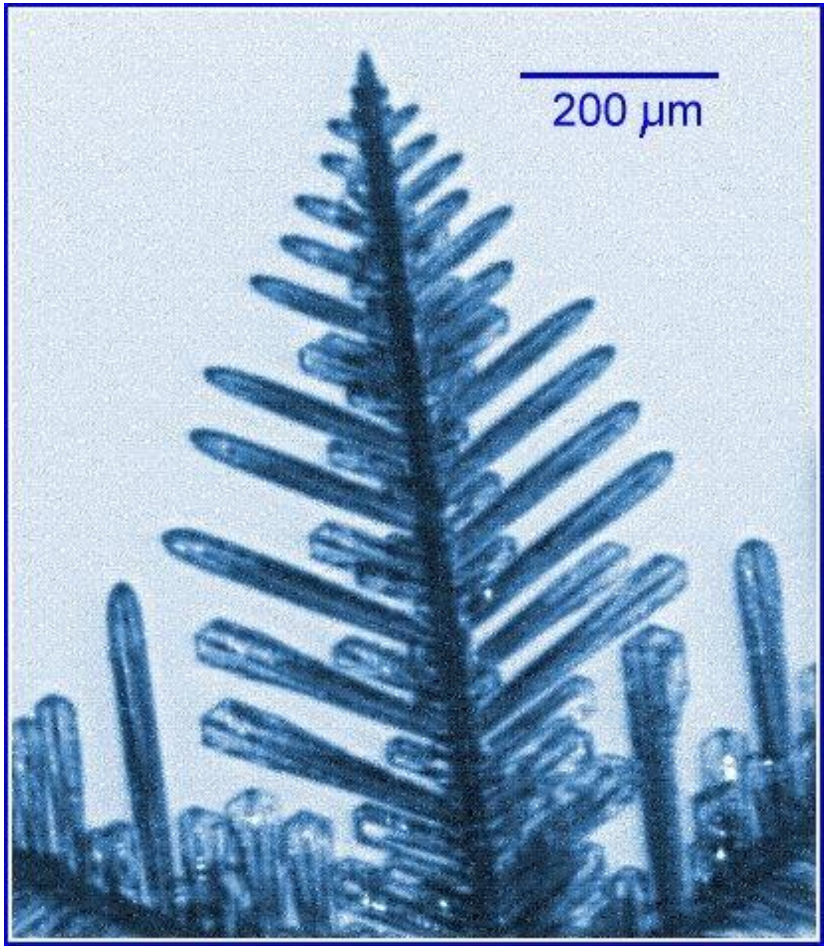
The lateral growth Mechanisms:

(A) Mononucleation

(B) Polynucleation

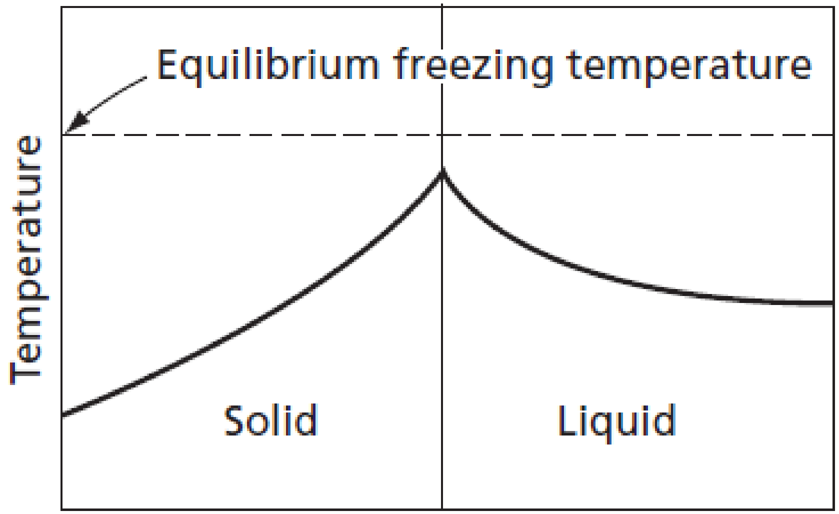
(C) Spiral growth

Growth of pure solid

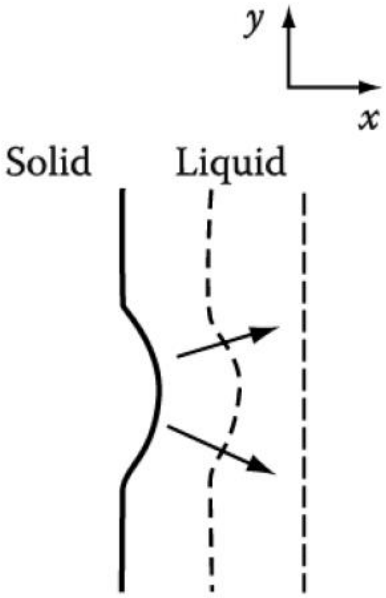


In pure metals, solidification is controlled by the rate at which the latent heat of solidification can be conducted away from the solid-liquid interface

Dendritic growth in pure metal

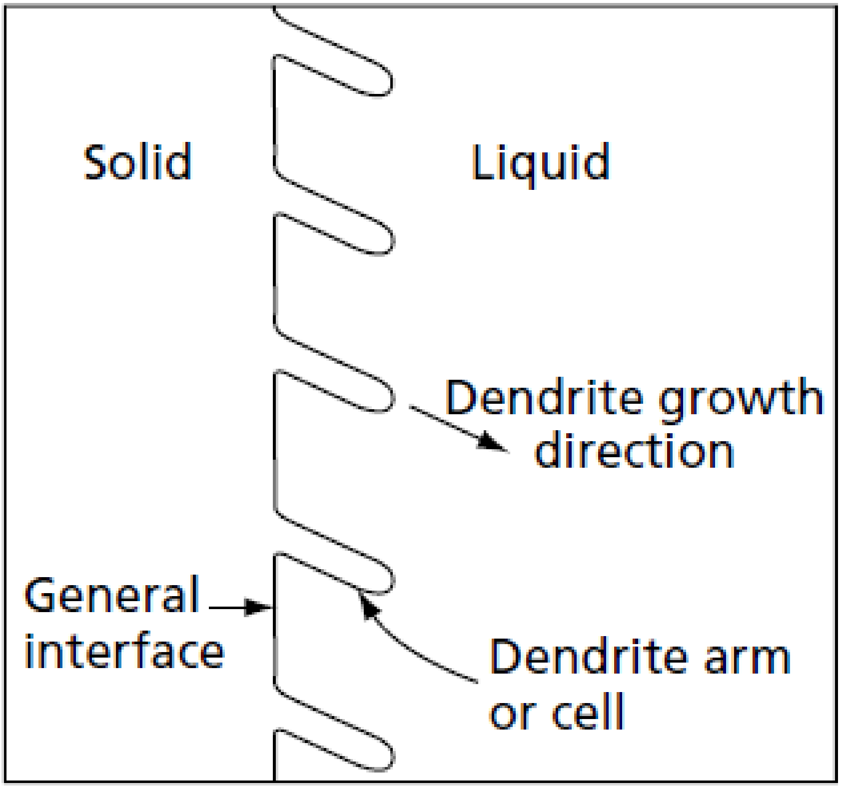


Temperature inversion during freezing



The temperature ahead of the protrusion is lower compared to surrounding. Thus heat flows from solid to undercooled liquid. The protrusion grows preferentially

Dendritic growth in pure metal



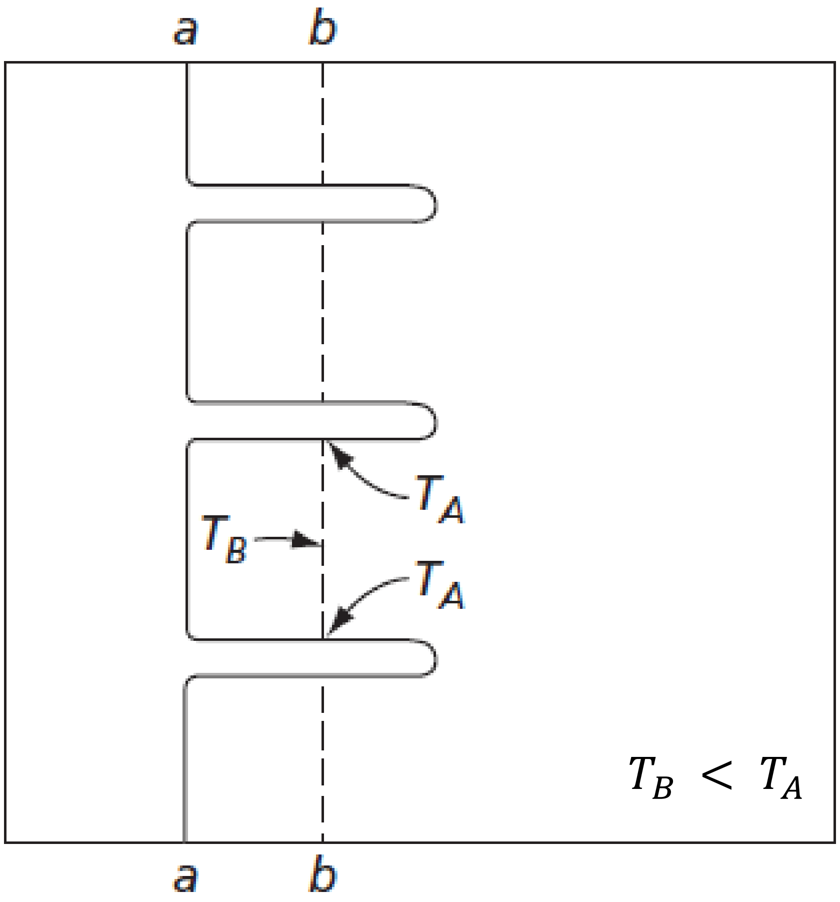
- The latent heat raises the temperature of the liquid adjacent to any given cell and retards the formation of other similar projections on the general interface in the immediate vicinity of a given projection
- The result is that a number of cells of almost equal spacing are formed that grow parallel to each other

Growth Direction

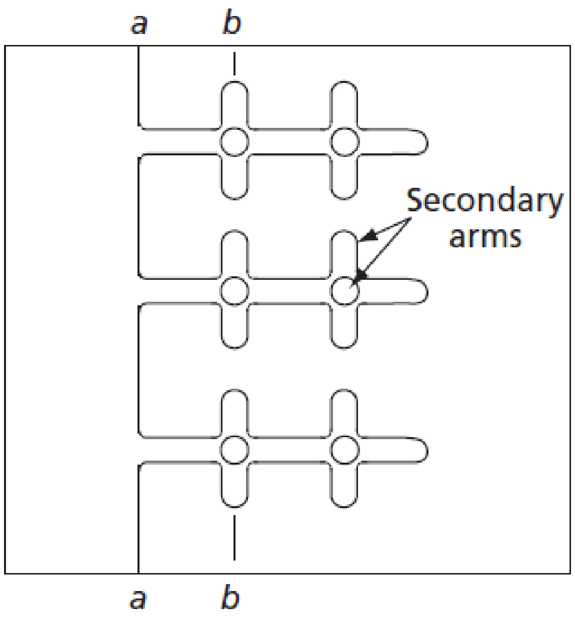
- Direction in which these cells grow is crystallographic
- This is known as the dendritic growth direction
- The direction of dendritic growth depends on the crystal structure of a metal

Crystal Structure	Dendritic Growth Direction
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)	$\langle 110 \rangle$

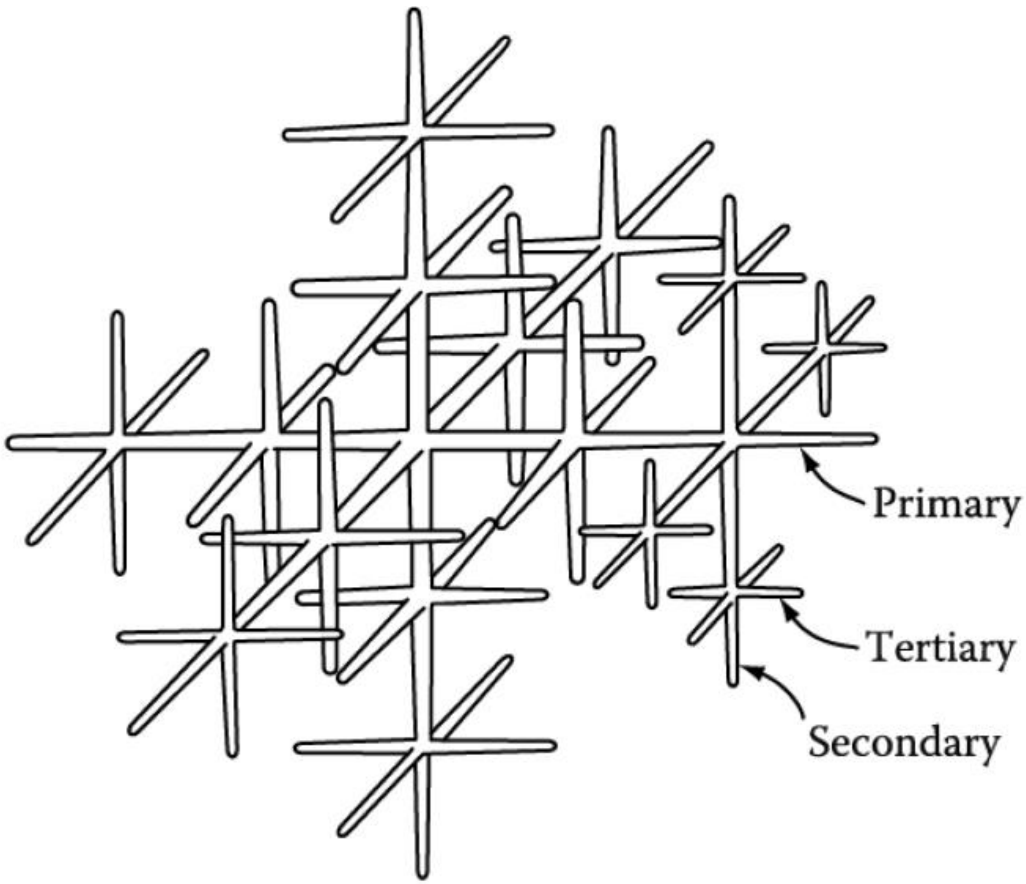
Secondary branches



Secondary dendrite arms form because there is a falling temperature gradient starting at a point close to a primary arm and moving to a point midway between the primary arms.

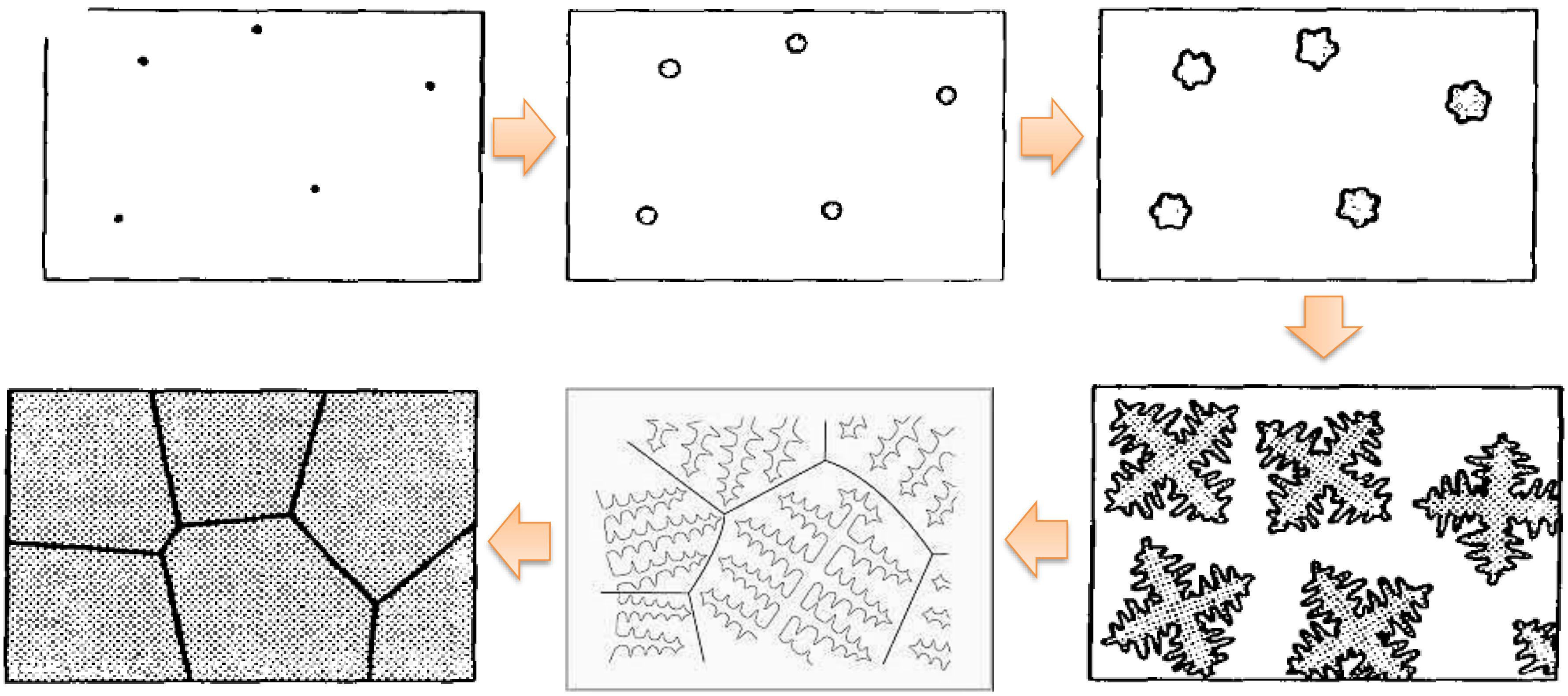


Dendritic structure

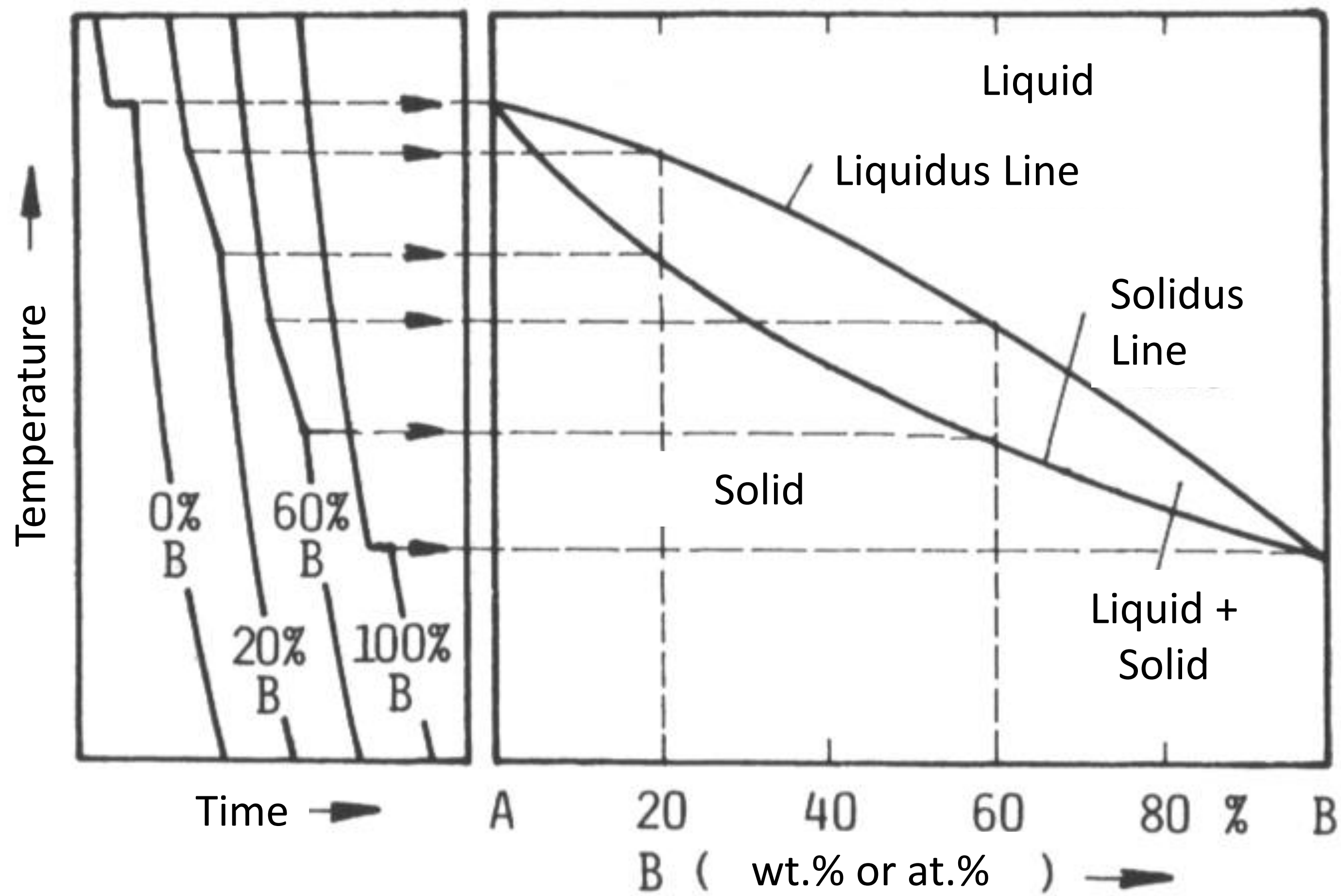


A dendritic crystal formed by three-dimensional dendritic growth

Growth of equiaxed dendrites

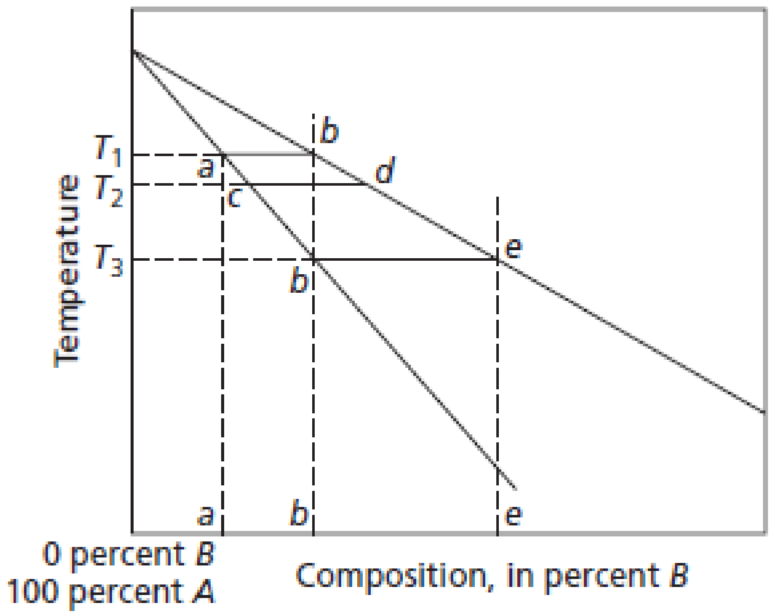


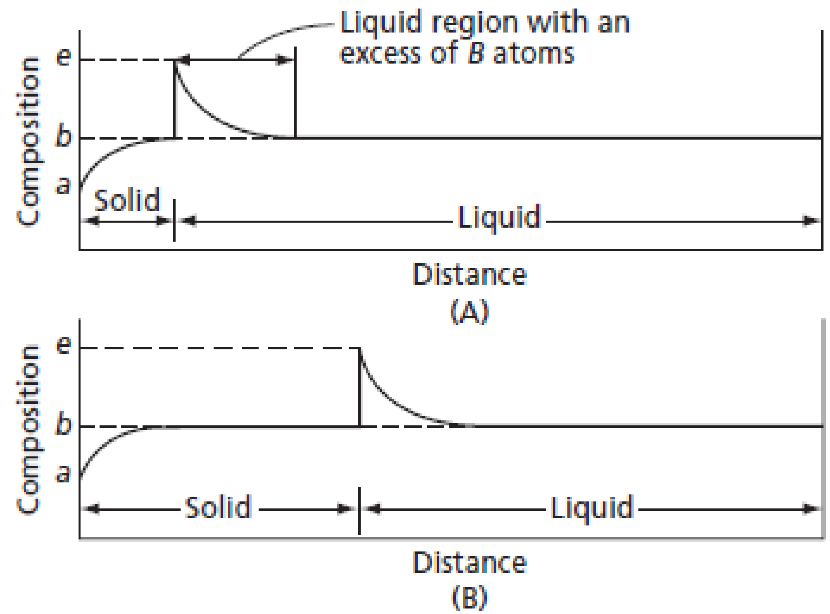
Binary alloy

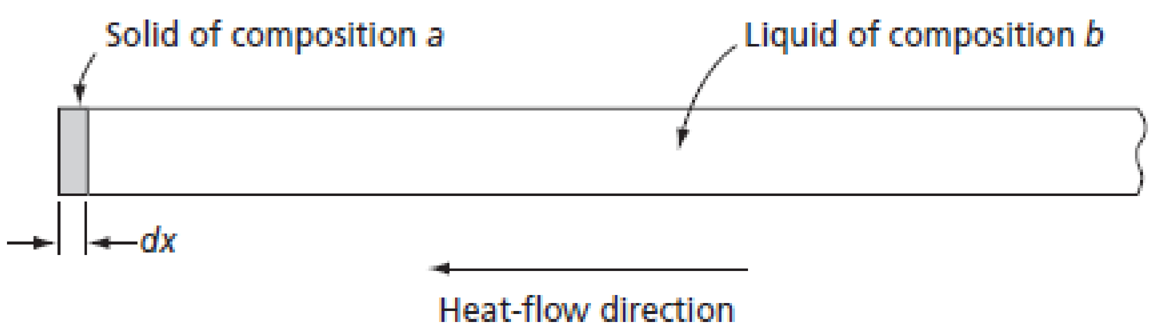


Unidirectional solidification of binary alloy

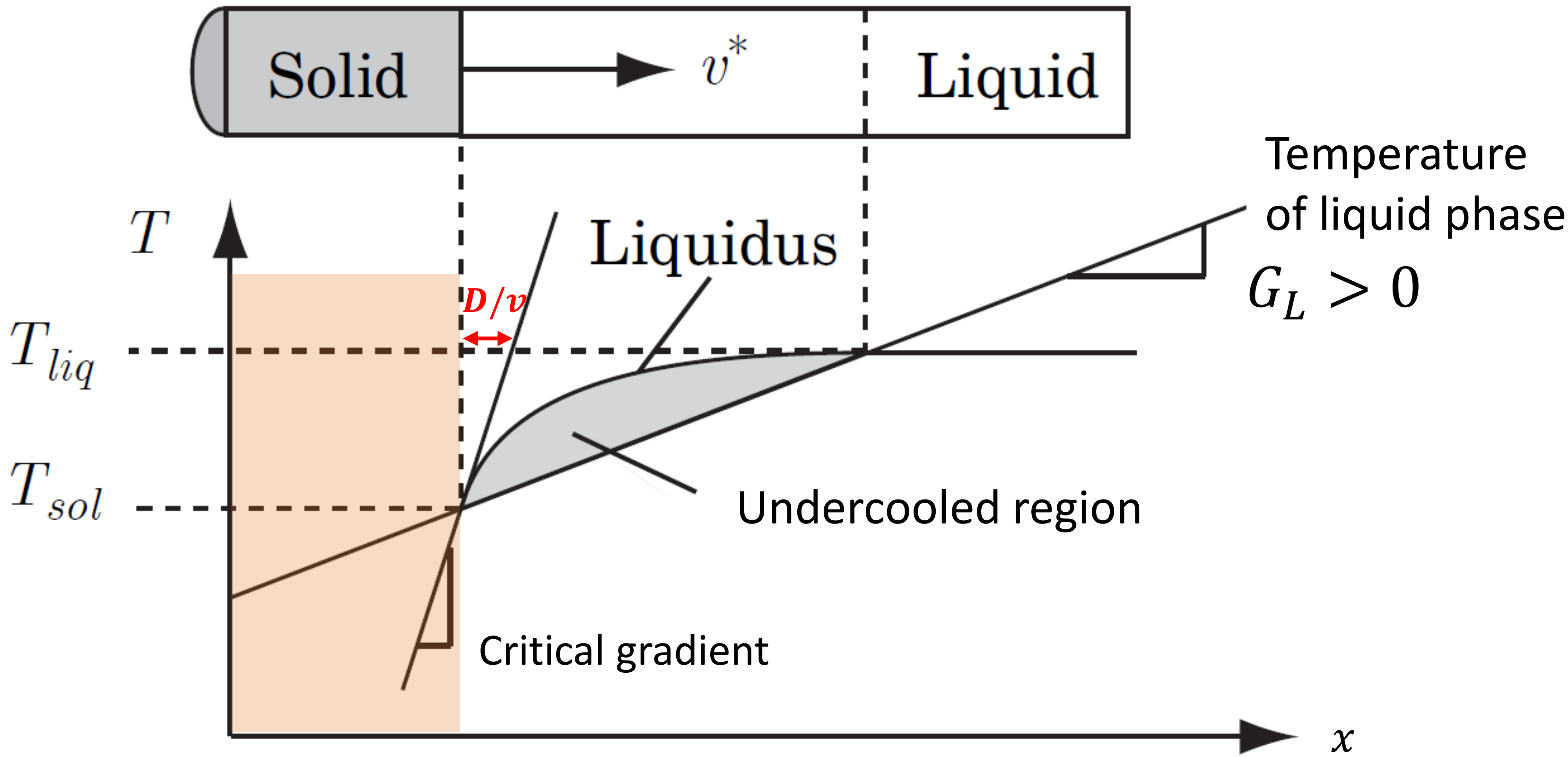
Isomorphous binary phase diagram





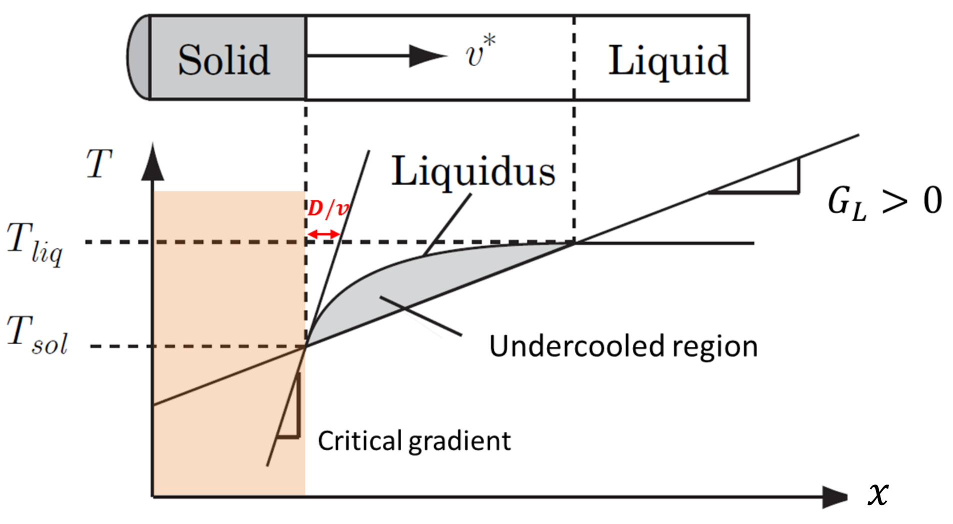


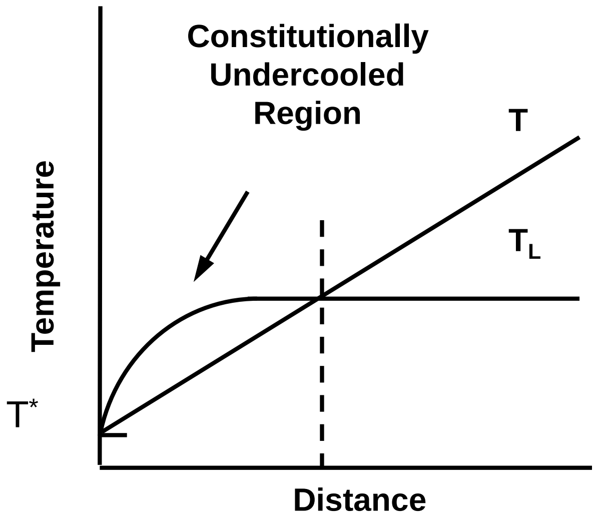
Dendritic freezing of alloy



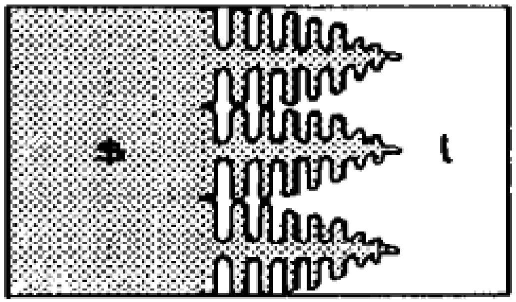
The liquid in front of the solidification front exists below its equilibrium freezing temperature, i.e. it is undercooled

Formation of stable protrusion on planar interface

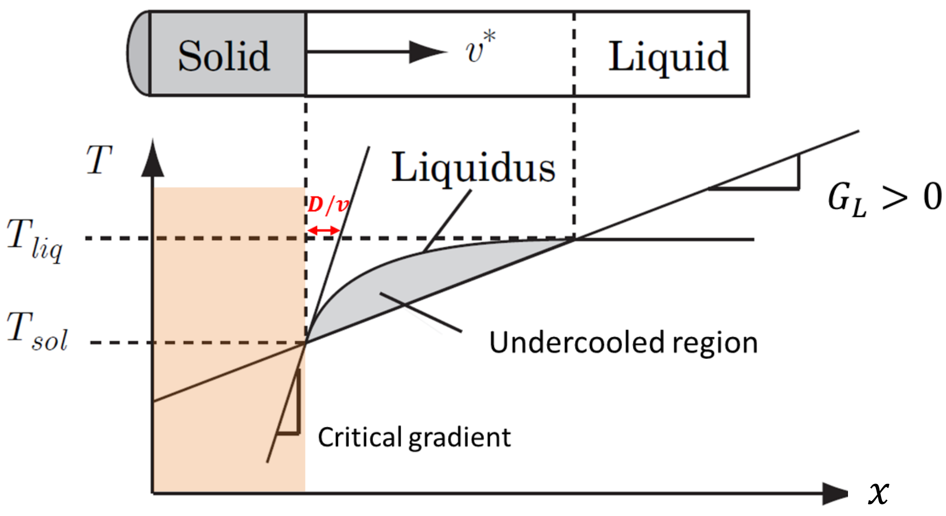


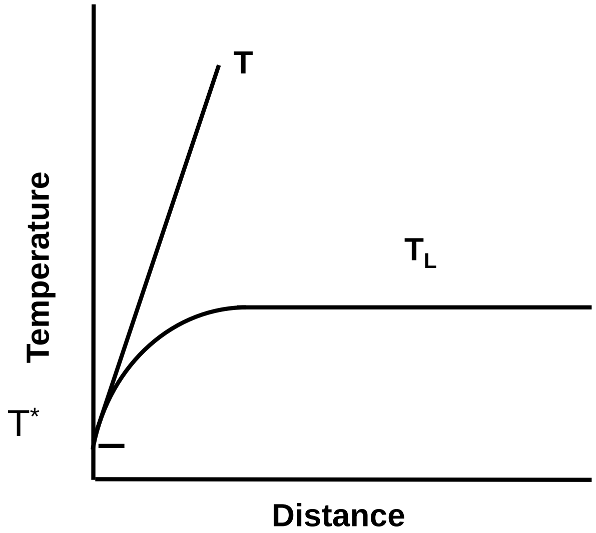


- Temperature at the tip of protrusion that forms will be higher than that of surrounding interface
- The tip remains below local liquidus temperature, thus protrusion can develop
- Planar interface is unstable



Formation of stable protrusion on planar interface



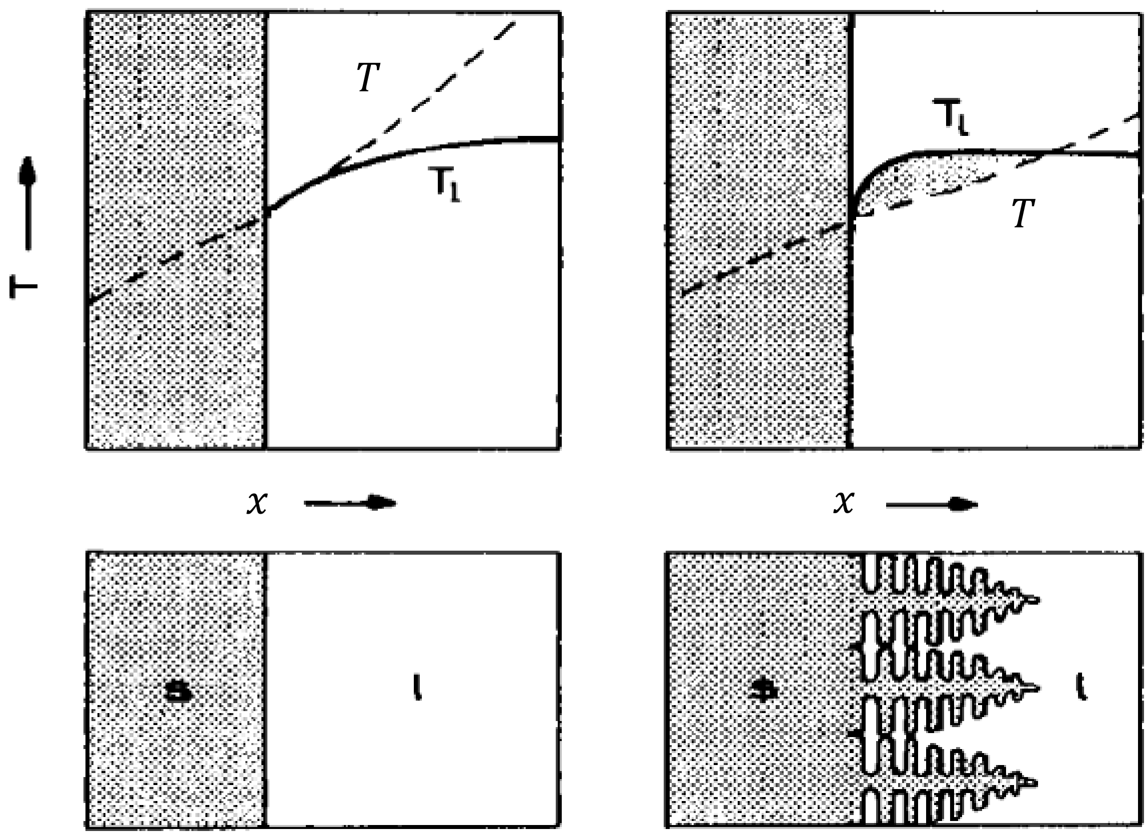


- The temperature gradient ahead of interface is steeper than the critical gradient
- The tip of protrusion will be raised above liquidus temperature and the protrusion will be melted back.
- Planar interface is stable

Resulting structures

$$\frac{G_L}{v} \geq \frac{-mC_0(1-k)}{kD}$$

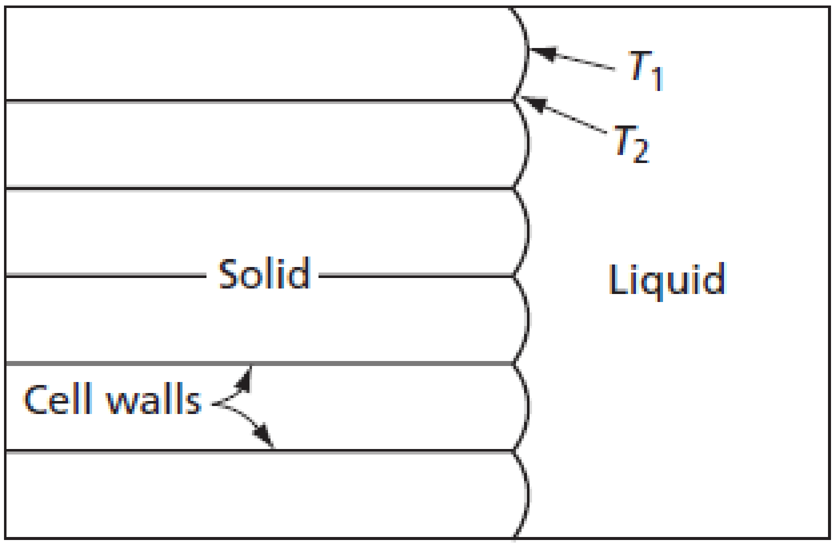
$$\frac{G_L}{v} < \frac{-mC_0(1-k)}{kD}$$

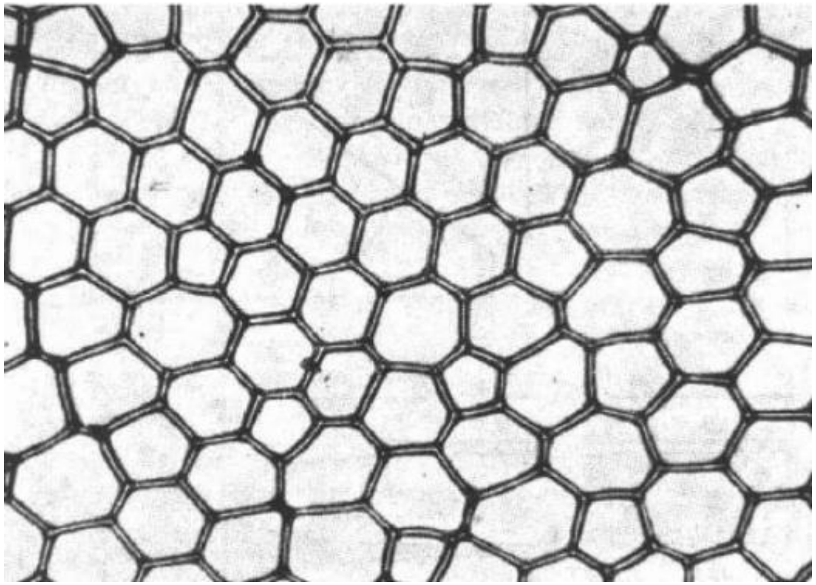


Breakdown of planar front with constitutional undercooling

Cellular microstructures

When the region of constitutional undercooling is narrow, a cellular structure may form as the result of the movement of a stable interface

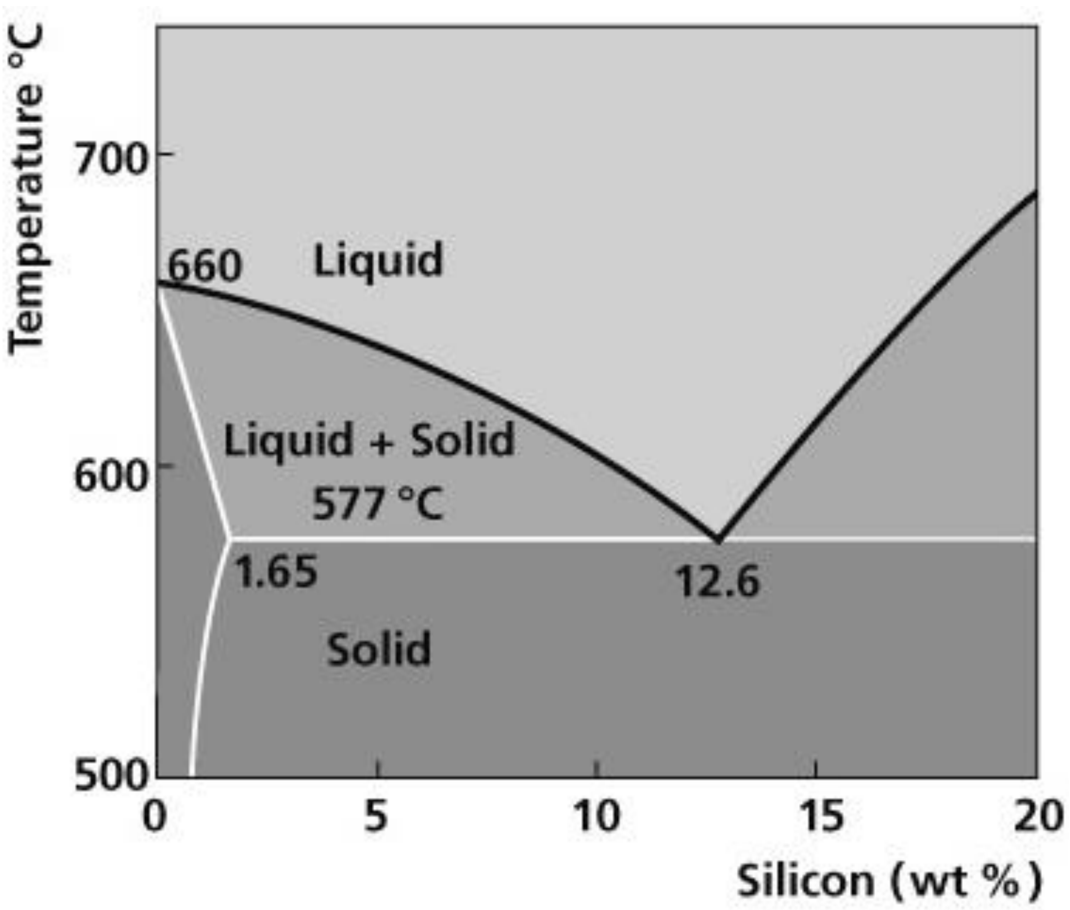


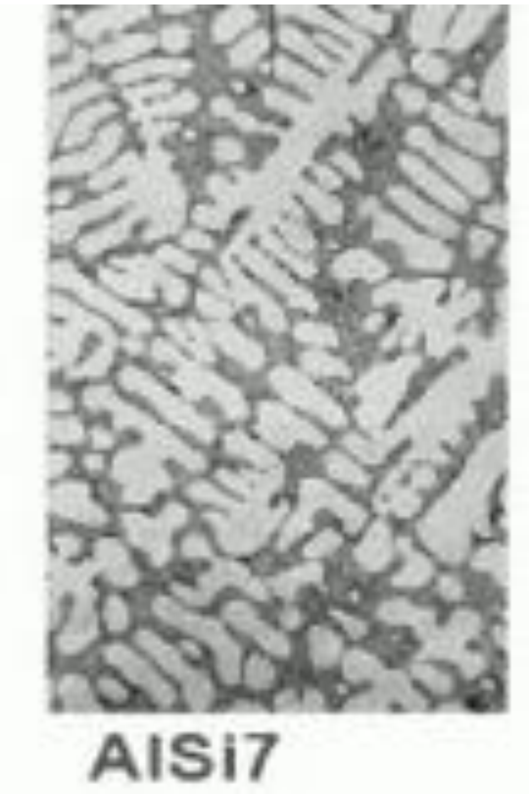


A decanted interface of a cellularly solidified Pb-Sn alloy (x 120)

(after J.W. Rutter in *Liquid Metals and Solidification*, American Society for Metals, 1958, p. 243)

Al-Si phase diagram



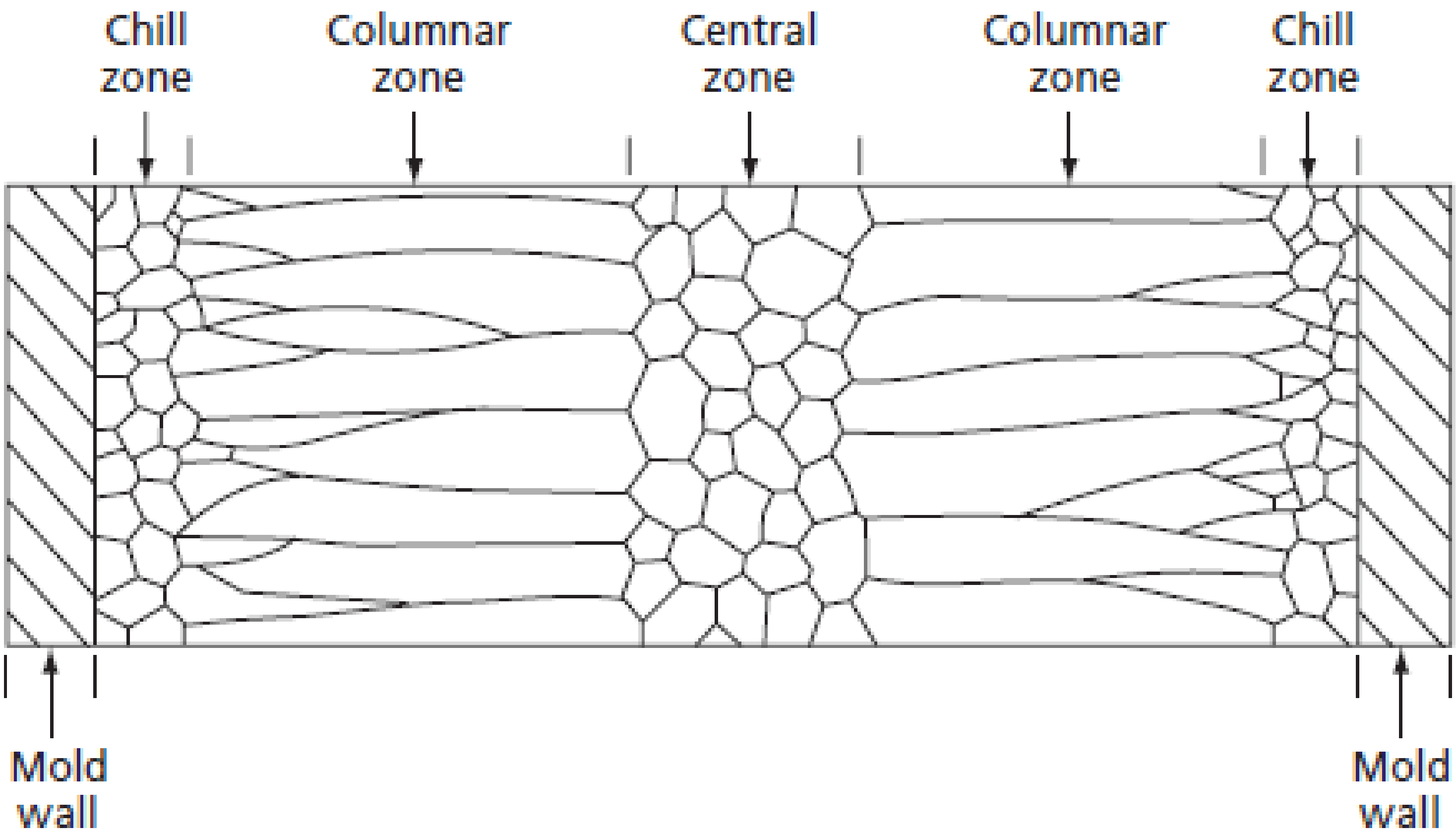


Freezing of ingot

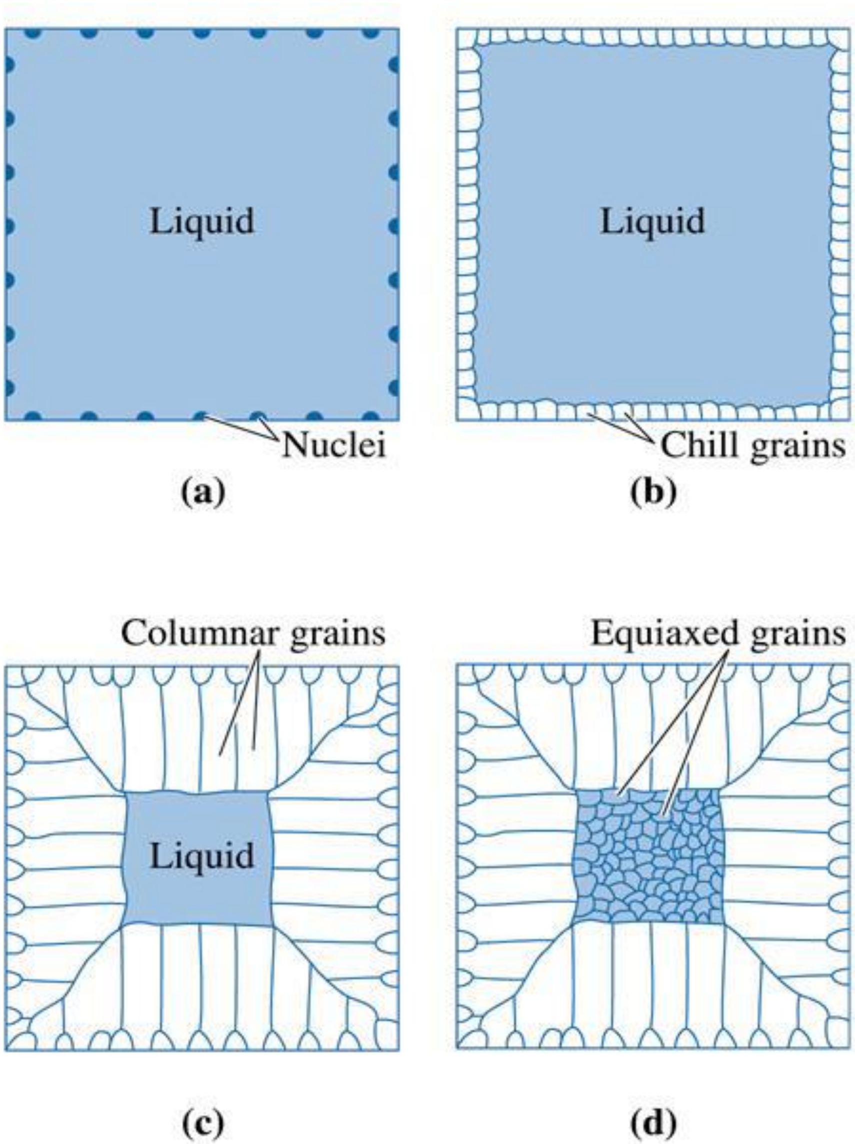
- Chill zone - A region of small, randomly oriented grains that forms at the surface of a casting as a result of heterogeneous nucleation.
- Columnar zone - A region of elongated grains having a preferred orientation that forms as a result of competitive growth during the solidification of a casting.
- Equiaxed zone - A region of randomly oriented grains in the center of a casting produced as a result of widespread nucleation.

Cast structure of ingot

Section through a large ingot, and the three basic zones of freezing that may be found in a casting



Cast structure of ingot



Development of the ingot structure of a casting during solidification:

- (a) Nucleation begins
- (b) the chill zone forms
- (c) preferred growth produces the columnar zone
- (d) additional nucleation creates the equiaxed zone

Rate of solidification

Heat flow during casting is a complex phenomenon and depends on several factors relating to material cast and the mould and the process parameters.

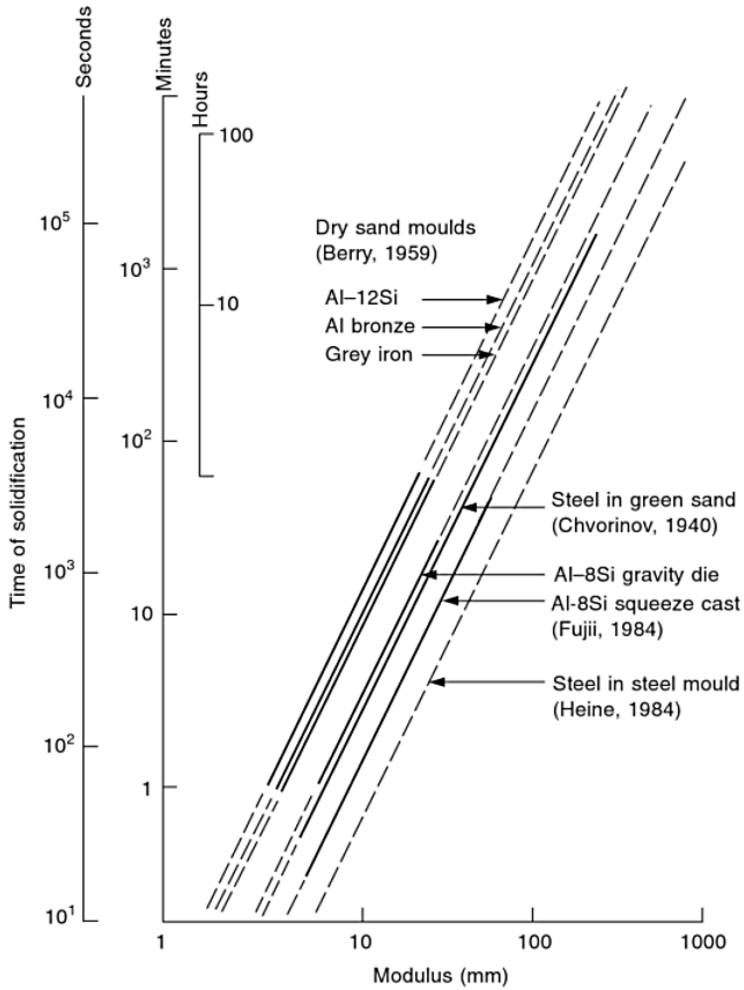
The **rate of solidification** of a metal during casting is dictated by

- The excess heat in the liquid metal (superheat liquid) on pouring
- The amount of heat produced by the solidification of the metal (the latent heat of fusion)
- The rate at which this heat can be dissipated from the metal (heat flow rate)

Why heat flow in casting is important?

(1) Determining time of solidification

Freezing time of plate-shaped casting in different alloys and moulds

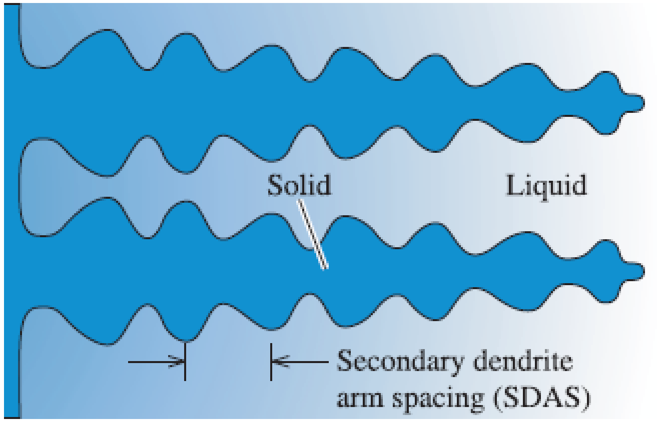


$$t_f = C\left(\frac{V}{A}\right)^n$$

$$n = 1 - 2$$

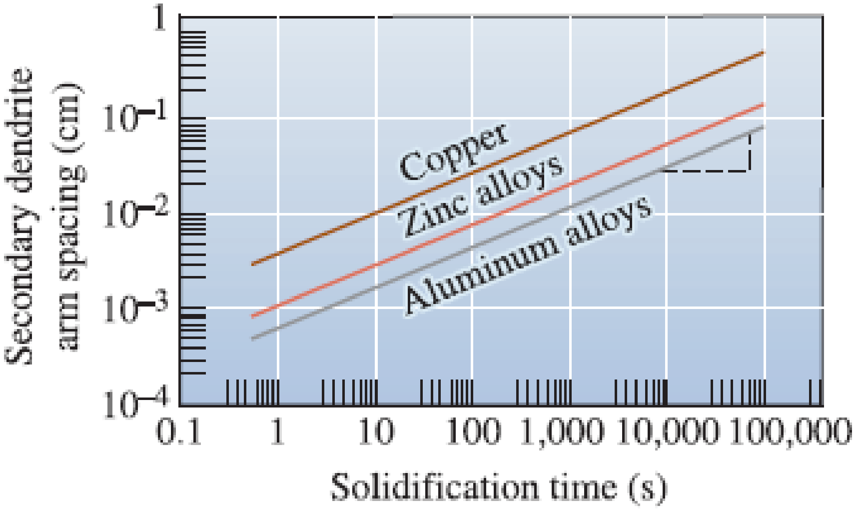
Effect on Structure and Properties

- Solidification time affects the size of dendrites.
- Dendrite size is normally characterised by measuring distance between the secondary dendrite arm (SDAS – secondary dendrite arm spacing).

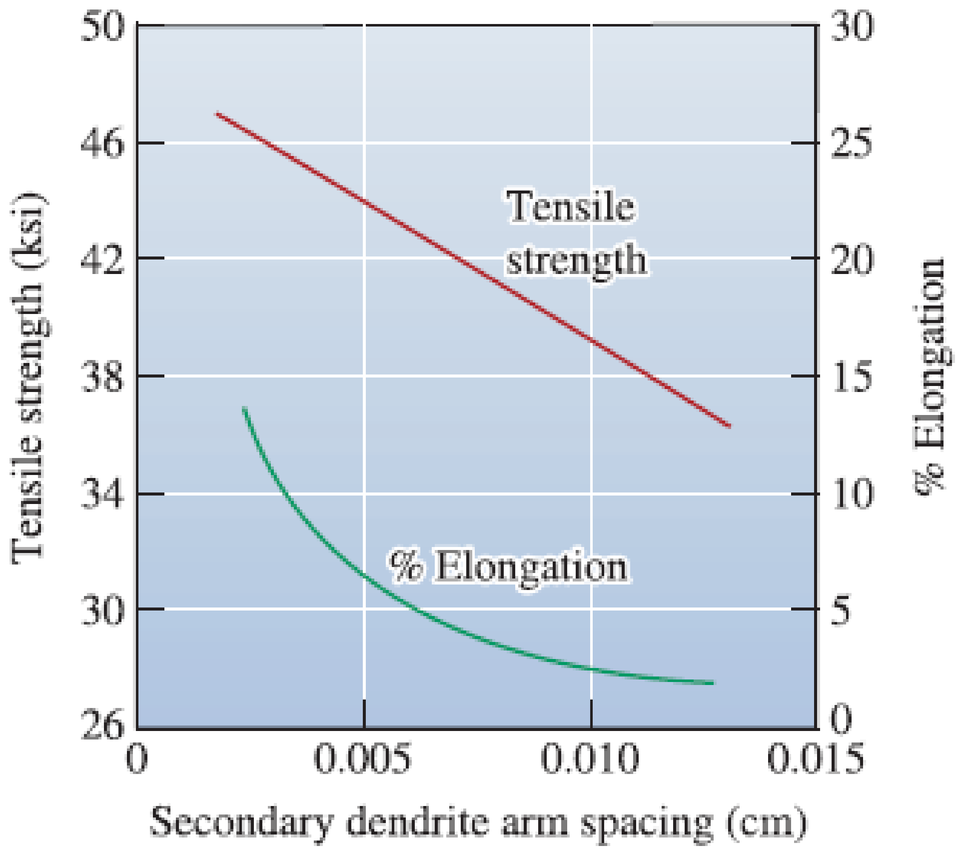


$$SDAS = k(t_f)^m$$

where *k* and *m* are constants depending on composition of metals



Effect on Structure and Properties

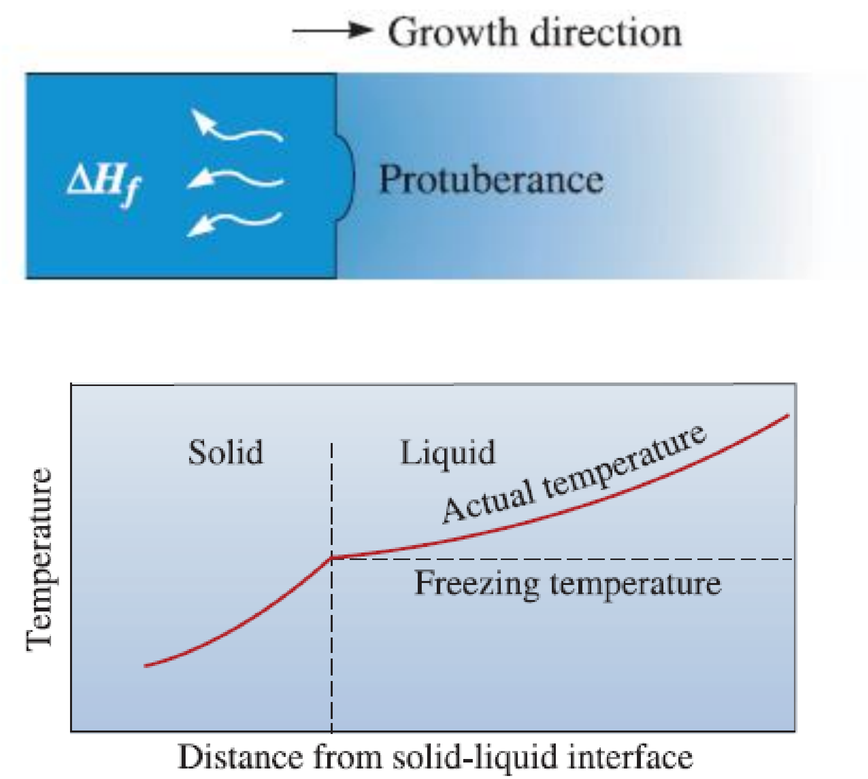


The effect of the secondary dendrite arm spacing on the mechanical properties of an aluminium casting alloy

Why heat flow in casting is important?

(2) Determining nature of the solid growth

Planar Growth



Dendritic Growth