

Chap. 4. Solidification.

- Solid'n & Melting - transf. bet'n Xtallographic & non-Xtallic stat of metls
- input casting, foundry, continuous casting ...
- objective : to develop the basic concept of solid'n.

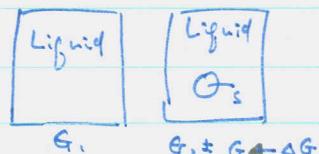
4.1. Nucleation in Pure Metals.

- Undercooled condition ($G_L - G_s$) : driving force but no spontaneous solid'n.
- " ^(EIC) need nuclei to start the transf. if ^{impurities} available
- Normally ^{lik} supercooling initiate the transf. \rightarrow heterogeneous nucleation
- A Large undercooling observed when no hetero-nuclei sites.
- homogeneously solid nuclei forms.

1. Homo. Nucl'n.

$$\text{Fig. 4.1. } G_2 = V_s G_v^s + V_L G_v^L + A_{SL} Y_{SL}$$

(f.E/unit vol.) interface f.E.



w/o any solid present.

$$G_1 = (V_s + V_L) G_v^L$$

\therefore Formation of solid \rightarrow cause $ΔG_i = G_2 - G_1$

$$(4.1) \quad ΔG = -V_s ΔG_v + A_{SL} Y_{SL}$$

$$(4.2) \quad (= G_v^L - G_v^s)$$

$$(4.3) \quad \text{For an undercooling } ΔT. \quad (1.17) \rightarrow \Delta G_v = \frac{L_v ΔT}{T_m} = \frac{\Delta H_fus}{T_m}$$

latent heat of fusion
unit vol.

when $T < T_m$

$$\Delta G_v > 0$$

$$\therefore \Delta G = -V_s \Delta G_v + A_{SL} Y_{SL}$$

$$= \frac{\Delta H_fus}{T_m} (T_m - T)$$

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neg. pos. $< 0 \rightarrow \text{固}$.

if γ_{SL} is isotropic \rightarrow sphere \hookrightarrow
and this has a radius r

$$(4.4) \Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}.$$

$$\text{Hence, } d\Delta G_r = (-4\pi r^2 \Delta G_v + 8\pi r \gamma_{SL}) dr$$

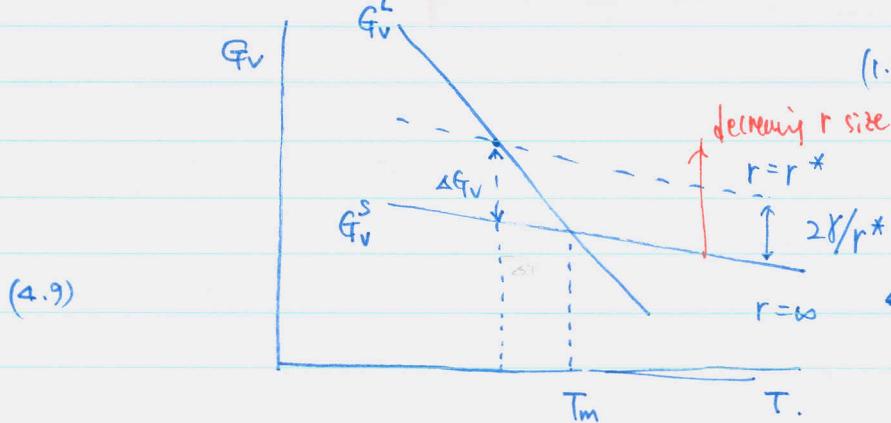
$$(4.5) \frac{d\Delta G_r}{dr} = 0 \text{ at equilibrium} \quad r^* = \frac{2\gamma_{SL}}{\Delta G_v}$$

$$(4.6) \Delta G_{\text{homo}}^* = -\frac{4}{3}\pi \left(\frac{2\gamma_{SL}}{\Delta G_v}\right)^3 \Delta G_v + 4\pi \left(\frac{2\gamma_{SL}}{\Delta G_v}\right)^2 \gamma_{SL}$$

$$= \frac{16}{3}\pi \frac{\gamma_{SL}^3}{(\Delta G_v)^2} = \frac{1}{2} \left[\frac{4}{3}\pi \cdot \left(\frac{2\gamma}{\Delta G_v}\right)^3\right] \Delta G_v = \frac{1}{2} V^* \cdot \Delta G_v$$

$$(4.7) \quad (4.5) + (4.6) \quad r^* = \frac{2\gamma_{SL}}{\Delta G_v} \leftarrow = \frac{L_v \Delta T}{T_m} \rightarrow r^* = \left(\frac{2\gamma_{SL} T_m}{L_v}\right) \frac{1}{\Delta T}$$

$$\checkmark (4.8) \quad (4.6) + (4.3) \quad \Delta G^* = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2}\right) \frac{1}{(\Delta T)^2}$$



$$(4.9) \quad \Delta G_r = \frac{2\gamma V_m}{r} / \text{mole.}$$

solid sphere \hookrightarrow difference
 \circlearrowleft bulk solid

$$\therefore \Delta G_v = \frac{2\gamma_{SL}}{r^*} / \text{volume.}$$

$$= (4.5)$$

4.4

- What's happening? during homo. nucleation. ($\ell \rightarrow s$)

$$= V \times (\gamma_{100} - \Delta \gamma)$$

- 2-4% vol. increase when $s \rightarrow l$. (more freedom of atoms)

- On avg., the # of spherical clusters of radius r before becoming solid!

$$(4.10) \quad N_r = N_0 \exp\left(-\frac{\Delta G_r}{kT}\right) \quad \text{the excess f.e. of cluster.} \quad (4.4)$$

Sensitive \checkmark
fn of size ($\Delta G_r = \frac{4\pi r^3}{3} \gamma_{SL}$) \downarrow
total # of atoms in the sys.

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Applied $\left\{ \begin{array}{ll} T < T_m & \text{for any } r \\ T \geq T_m & \text{for } r \leq r^* \\ & \text{cluster liquid} \\ & \text{if } r > r^* \text{ only solid!} \end{array} \right.$

$$(4.4) + (4.10) \quad \Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 Y_{SL}$$

$$N_r = N_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

ex1. Cu.

in a given vol. (1 mm^3) at T_m $\rightarrow N_0$ ($\approx 10^{20}$ atoms)

$\rightarrow N_r (\approx 10^{14})$ if $r, \Delta G_v, Y_{SL}$ known.
cluster size of 0.3 nm (60 atoms) $\approx 7 \times 10^{13}$ cluster

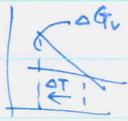
if $r = 0.6 \text{ nm}$ (60 atoms) $N_r \approx 10$

This ex. shows how sensitively cluster density depends on their size.

ex2. Other than T_m .

i) $T < T_m$ the contribution of $\Delta G_v \uparrow$ in Eq. (4.4). \uparrow

$$\Delta G_r = -VAG_v + A\Delta f_p \frac{T}{T_m}$$



\rightarrow chance to have a cluster of $r > r^*$

of ΔG_r nucleation (for example 1 cluster/ mm^3 as in the ex1)

$$N_r = N_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

$$\Delta G_{r,m} \text{ is const } (= -\frac{4}{3}\pi r_m^3 \Delta G_v + 4\pi r_m^2 Y_{SL})$$

$$\frac{4\pi r_m^2 Y_{SL}}{kT_m}$$

2. Hetero. The Homo. Nucl'n Rate.

How fast solid nuclei will appear in the liquid at a given undercooling

of crit. size cluster ($10^{29} \text{ atom}/\text{m}^3$)

$$(4.11) \quad C^* = C_0 \exp\left(-\frac{\Delta G_{\text{homo}}^*}{kT}\right) \quad \text{clusters/m}^3$$

for the phenomenon that the addition of 1-2 atoms to those cluster will cause nuclei to grow.

$$(4.12) \quad N_{\text{homo}} = f_0 \cdot C^* \quad \text{nuclei/m}^3 \cdot \text{sec}$$

freq. factor ($\approx 10^{11}$) $f_0 = f$ vib. freq. of the atoms, ΔG^* for diff. intg., the surface area of the crit. nuclei) activation E

\Rightarrow A reasonable nucl. rate ($1/\text{m}^3 \cdot \text{sec}$) is obtained

when $\Delta G^* = \sim 78 \text{ kJ/mol}$

(4.13)

$$N_{\text{homo}} = f_0 C \exp \left(- \frac{A}{(\Delta T)^2} \right)$$

$$\Delta G^*_{\text{homo}} = \frac{16\pi}{3} \frac{\gamma^3}{(\Delta G)^2}$$

$$= \frac{16\pi}{3} \frac{\gamma^3}{L_v^2} \frac{T_m^2}{(\Delta T)^2}$$

$$\text{where } A = \frac{16\pi \gamma_{SL}^3 T_m^2}{3 L_v^2 k T}$$

insensitive to temp.

 N_{homo}

Fig 4.6.

ΔT_N
non nuclei

rapid rise. (explosion of nuclei)

* Turnbull $\Delta T_N \sim 0.2 T_m$ ($\sim 200^\circ\text{C}$ for most metal) ΔT .* (4.13) + ΔT_N → to calculate γ_{SL} in Table 3.4

p170!

measured value

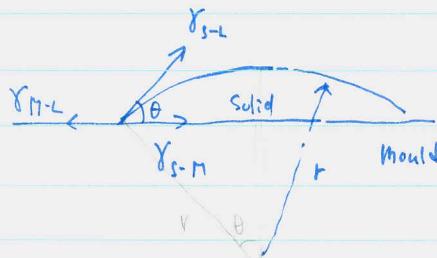
* homo nucleation rate, hetero nucleation common in solid'n.

crevice at
on mould wall, impurity.

3. Hetero Nucleation.

$$(4.8) \quad \Delta G^* = \left(\frac{16\pi \gamma_{SL}^3 T_m^2}{3 L_v^2} \right) \frac{1}{(\Delta T)^2}$$

- Nucleation becomes easy if $\gamma_{SL} \downarrow$ - by forming nucleus from mould wall.

- assuming γ_{SL} isotropic.

for a given vol. total interfacial E of the sys. is min. if the embryo is in a spherical cap form.

$$\gamma_{ML} = \gamma_{SL} \cos \theta + \gamma_{SM}$$

(4.14)

$$\cos \theta = (\gamma_{ML} - \gamma_{SM}) / \gamma_{SL}$$

$$\Delta G_{\text{het}} = -V_s \Delta G_v + A_{SL} \gamma_{SL} + A_{SM} (\gamma_{SM} - \gamma_{SL})$$

Ex 4.6.

$$A_{SL} = 2\pi r^2 (1 - \cos\theta)$$

$$A_{SM} = \pi r^2 \sin^2\theta$$

$$V_s = \frac{\pi r^3}{3} (2 + \cos\theta) (1 - \cos\theta)$$

$$(4.16) \quad \Delta G_{het} = \left\{ -\frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 Y_{SL} \right\} S(\theta)$$

$$(4.17) \quad \text{where } S(\theta) = \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{c} \leq 1$$

Shape factor

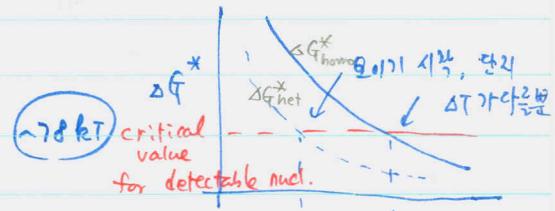
differentiate (4.16)

only affected by ΔT !! $(= \frac{2\delta V_m}{L_v} \cdot \frac{1}{\Delta T})$

$$(4.18) \quad \frac{\partial \Delta G_{het}}{\partial T} = 0 \rightarrow r_{het}^* = \frac{2Y_{SL}}{\Delta G_v} \rightarrow \text{homo \& hetero } r^* \text{ the same : } r^* \text{ indep. of nucle. sites}$$

$$(4.19) \quad \Delta G_{het}^* = \frac{16 \pi Y_{SL}^3}{3 \Delta G_v^2} \cdot S(\theta) : \Delta G_{het}^* \text{ is smaller than } \Delta G_{homo}^* \text{ by } S(\theta)$$

$$(4.20) \quad \Delta G_{het}^* = S(\theta) \Delta G_{homo}^*$$

ex. when $\theta = 10^\circ$ $S(\theta) \approx 10^{-4}$ $\theta = 30^\circ$ $S(\theta) \sim 0.02$ $\theta = 90^\circ$ $S(\theta) = 0.5$ - The effect of ΔT on ΔG_{het}^* & ΔG_{homo}^* . n_1 atoms in contact w/ the mould wall

$$(4.21) \quad \text{the # of nuclei: } N^* = n_1 \exp \left(-\frac{\Delta G_{het}^*}{kT} \right)$$

$$(4.22) \quad N_{het} = f_i C_i \exp \left(-\frac{\Delta G_{het}^*}{kT} \right) \quad f_i: \text{freq. factor.}$$

 C_i : # of atoms in contact w/ hetero- Nucleation inside crevices. \downarrow (ΔG_{het}^*)

nucl. sites/unit vol. of liquid.

$$(4.23) \quad \Delta G^* = \frac{1}{2} V^* \Delta G_v$$

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(Cap or sphere)

This eq. & (4.7) $r^* \propto \frac{1}{\Delta T}$ is quite generally true for any nucleation.

1. For surface nucleation

→ equilibrium shape of ppt was a disc type

(100)

height $\approx 10 \text{ \AA}$

$$\gamma_{coh} = 100 \text{ mJ/m}^2$$

Diameter 100 \AA

$$\gamma_{coh} = ?$$

happen w/ the initial thickness of the cluster

(* atom layers thick.)

00000

w/ known ΔT_i

{ calculate r^* .
Set-up assumption.

2. Spiral Growth

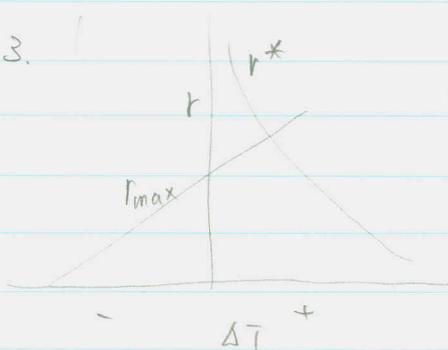
screwed per dist. of min radius? $\Delta G_v = V\Delta G_v + A\gamma$ when $= 0$. melting solidification

$$\Delta G_v = G^l - G_s \quad (r = \infty)$$



$$\Delta G_v = + V \cdot \Delta P \quad (r = r^*)$$

3.



Why $r_{max} \uparrow$ as $\Delta T \uparrow$

- if \Rightarrow a nucleus form at the root of a crack V^* is very small
+ $\Delta G^* \downarrow$ even if θ is large.
when $\theta = 90^\circ$: nucleation from cracks w/ very small ΔT . & θ is large
- For the crack to be useful for nucleation the crack opening must be large so that it can grow out. w/o the radius of s-l interface
 \swarrow 적당한 크기. 적당히 \downarrow decreasing ΔG^*
- In commercial practice use of inoculatit to the melt forms a solid comp - acts as abet. site. to refine the final g. structur.

4. Nucleation of melting.

$$(4.24) \quad \gamma_{sl} + \gamma_w < \gamma_{sv} \quad \text{Commonly.}$$

γ_{sl} is constant at T_m



$$\gamma_w = \gamma_{w, \text{pure}} + \gamma_{se}$$

$\therefore \theta = 0$, no superheating required for nucleation of liquid (melting)

(4.24) implies that a thin liquid layer can form below T_m . (why)

\rightarrow mechanism of melting is not properly understood !!.

- The solid \rightarrow melt transf. = increase in vac. conc. by $\sim 10\%$.

4.2. Growth of a Pure Solid.

two type of s-l interface

continuous growth (1) an atomically rough or diffuse interface. (in metallic)
lateral growth process (2) " flat or sharply defined interface. (non-m.)

1. Continuous Growth.

s/l diffuse interface \simeq migration of a random h.-angle p.b.



$\downarrow \Delta G^*$ \rightarrow needed. (diffusion in the lig.)

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✓ (4.25) the driving force for solid'n $\Delta G = -\frac{L}{T_m} \Delta T_i$ — undercooling at the interface.

(4.26)

✓ the net rate of solid'n $V = k_1 \Delta T_i$

$\Delta T_i \approx$

↳ related to boundary mobility : high value!!

∴ at T_m and $\frac{L}{T_m}$ with k_1

∴ w/ small $\Delta T_i \rightarrow$ solid'n occurs at T_i minor.

- pure metal grow at a rate controlled by heat conduction $\left. \begin{array}{l} \text{heat diffusion} \\ \text{by solute diffusion} \end{array} \right\} \text{diffusion control overall!!}$
- alloy " "

For diffuse interface

- Atoms can be received at any site on the solid ~~int~~ surface

(3.22) A : accommodation factor = 1. \rightarrow continuous growth
 \therefore interface not ordered & atoms arriving at random sites

not disturbing the equil^m

\rightarrow When interface smooth \rightarrow situation complex!!

2. Lateral Growth

Jackson's Theory $\frac{L_f}{T_m} > \frac{\text{smooth}}{4R}$

$$(AS_m = \frac{\Delta H_m}{T_m}) \Rightarrow (\text{why } \Delta G_m = 0 = \Delta H_m - T_m \Delta S_m)$$

$\frac{L_f}{T_m} \approx 12$ diffus

- Matls w/ a high entropy of melting prefer to form atomically smooth, close-packed interfaces
- For this interface, $G_{min} = U_{min} + PV - TS$ i.e., min. # of broken 'solid' bonds.

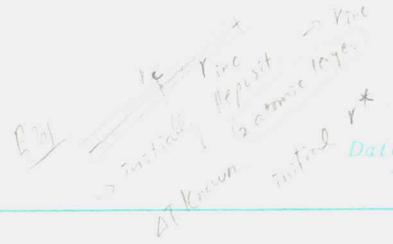
Fig 4.11 # of broken bonds
 a) flat surface 4 times \rightarrow back to figure
 for a single atom as b) ledge 2 times
 a cube depositing on c) corner 1 times; no increase
 the surface as → cause the lateral growth of ledges.

- Three ways to have lateral growth.

i) surface nucleation (repeated) ii) spiral growth iii) twin boundary

i) Surface Nuclein (repeated)

⑥



- If large # of atoms \rightarrow form a disc-shaped layer, then self-stabilized and continue to grow.



- the edges of disc + contribution to E \rightarrow counterbalanced by ΔG_V .
- ΔT become large, $r^* \downarrow \leftarrow$ critical $r(r^*)$ for 2-D disc shape nucleus

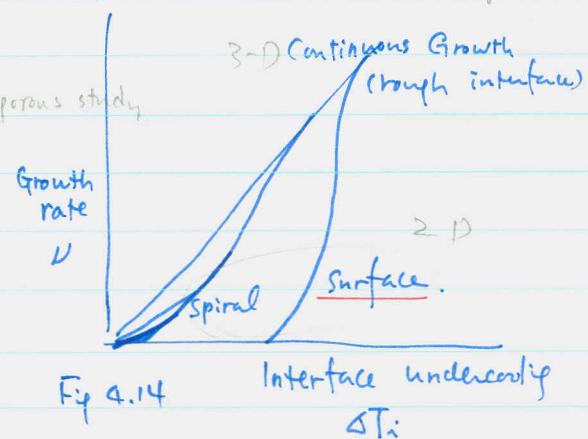
$$r^* = \frac{2\pi k_B}{L_V} \cdot \frac{1}{\Delta T}$$

const.

(4.27)

$$V \propto \exp(-k_2/\Delta T_i) \text{ after rigorous study}$$

- Very ineffective w/ small undercooling where r^* is large.



ii) Spiral Growth

Fig 4.14

Interface undercooling
 ΔT_i

- The addition of atoms to the ledge cause it to rotate around the axis of screw \perp .



- The spiral tightens until it reaches a min radius of r^*
 $r^* - \text{equil}^m$ w/ surrounding liquid. then all grow at the same speed.

$$\Delta G_V = \frac{2\theta}{r} \quad \uparrow \Delta G_V = \text{const}$$

(core & outer)

$$- V \text{ (growth rate)} = k_2 (\Delta T_i)^2$$

⑦

- Continuous growth, for a given V , has least ΔT_i
Surface growth max. ΔT_i

* Spiral Mech is important since repeated surface Nuclein less likely.

iii) Growth from Twin Boundary. (

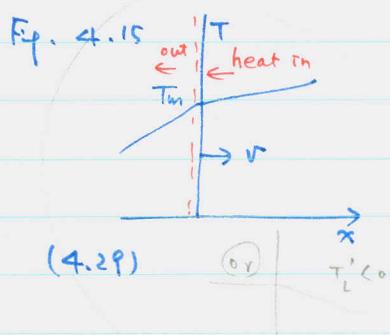
Another permanent source of steps!! like spiral growth.



3. Heat flow and Interface Stability.

- Pure metal: solidin controlled by heat conduction away from s/l interface
latent heat, ΔH_{trans}

Conduction thru the solid or the liquid depends on the T grad. at the interface



i) no supercooling.

- Solid growing at V (planar)

heat flow away from the interface thru solid

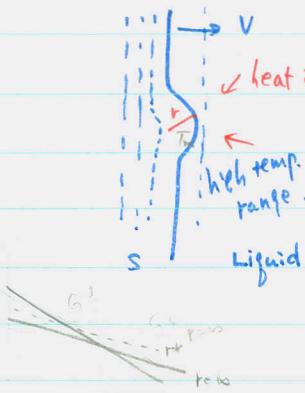
$$= \text{heat inflow from liquid} + L$$

$$K_s T_s' = k_L T_L' + \nu L v \quad \text{unit area!}$$

$$\begin{aligned} \text{therm. condue. } &\downarrow \\ \frac{\text{J}}{\text{cm} \cdot ^\circ\text{C} \cdot \text{s}} & \quad \frac{\text{d}T}{\text{dx}} \text{ solid.} \\ & \quad ^\circ\text{C/cm.} \end{aligned}$$

$$\begin{aligned} &(\text{m/sec} \cdot \text{J/cm}^2) \\ &(\text{m}^2) \end{aligned}$$

- Interface Instability. (Regular mould)



- If v is so large that G-Thompson effect can be ignored
the S-L interface remain at T_m .

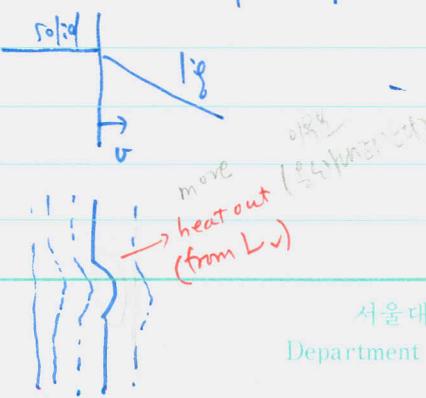
$T_s' \approx T_m$ more negative.

- $\therefore \frac{dT}{dx}$ in the liquid ahead of the protrusion will be increased (more positive) to balance. $\therefore \frac{dT_L'}{dx} > 0$ (0.19)

\therefore More heat to the protrusion \rightarrow melt away
 v to match other v of planar region.

ii) With supercooling

Fy 4.16 - A solid growing into supercooled liquid. (diff. from Instability).



- the protrusion $\frac{dT_L'}{dx} < 0$ becomes more negative!

\therefore heat flow from solid + the protrusion grows preferentially.

- Constitutional Supercooling. ^{(in alloy (4) NiA)} → perturbation will grow.

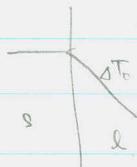
Nucl. at impurities

- * Shown at the beginning of solidification ^{at the tip of dendrites.}
 (if nucleation occurs at impurity conc.)

first solid, needs supercooling to grow.
 latent heat out.

- * Dendrites primary, secondary, tertiary arms : thermal dendrite
 bcc, fcc $\langle 100 \rangle$ growth orientation, help $\langle 1\bar{1}00 \rangle$ (pure metal)

- Dendritic growth & Heat conduction.



$$(4.29) \quad K_s T'_s = K_L T'_L + \nu L_v.$$

Assume $T'_s = 0$ T'_L measured in the direction of $L(T_L - \frac{\Delta T_c}{r})$

$\Delta T_c = -(T_\infty - T_i)$
 const. supercooling (impurity)
 actual supercooling

$\nu = -\frac{K_L T'_L}{L_v} \approx \frac{K_L \cdot \Delta T_c}{L_v r}$

$\Delta T_c = \frac{\Delta G_K}{r} = \frac{\Delta U_m}{r} = \frac{L_v \Delta T_r}{T_m}$

$\nu = \frac{K_L}{L_v r} \Delta T_r$ (4.30)

$\Delta T_r = \frac{2 \pi T_m}{L_v r}$ as a result of G-T eq.

$\nu \uparrow$ as $r \downarrow$ due to enhanced heat conduction (means $\frac{\Delta T_c}{r} = T'_L \uparrow$)

- min. radius r occur when $\Delta T_r = \Delta T_o = T_m - T_\infty$

$$r_{\min} = \text{the crit. nucle. radius } r^* = \frac{2 \pi T_m}{L_v \Delta T_o}$$

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

$$(4.31) \quad \nu = \frac{K_L}{L_v} \frac{1}{r} \left(1 - \frac{r^*}{r} \right) \Delta T_o \quad \text{since } \Delta T_o = \Delta T_c + \Delta T_r.$$

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- $\nu \rightarrow 0$ as $r \rightarrow r^*$ (G-T) and as $r \rightarrow \infty$ heat cond. slow. $\nu_{\max} = \frac{2 \pi T_m}{L_v r^*}$