2009 fall

Advanced Physical Metallurgy

"Phase Equilibria in Materials"

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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 ↑

$$N_{\text{hom}} \approx f_0 C_o \exp\{-\frac{A}{(\Delta T)^2}\} \sim \frac{1}{\Delta T^2}$$

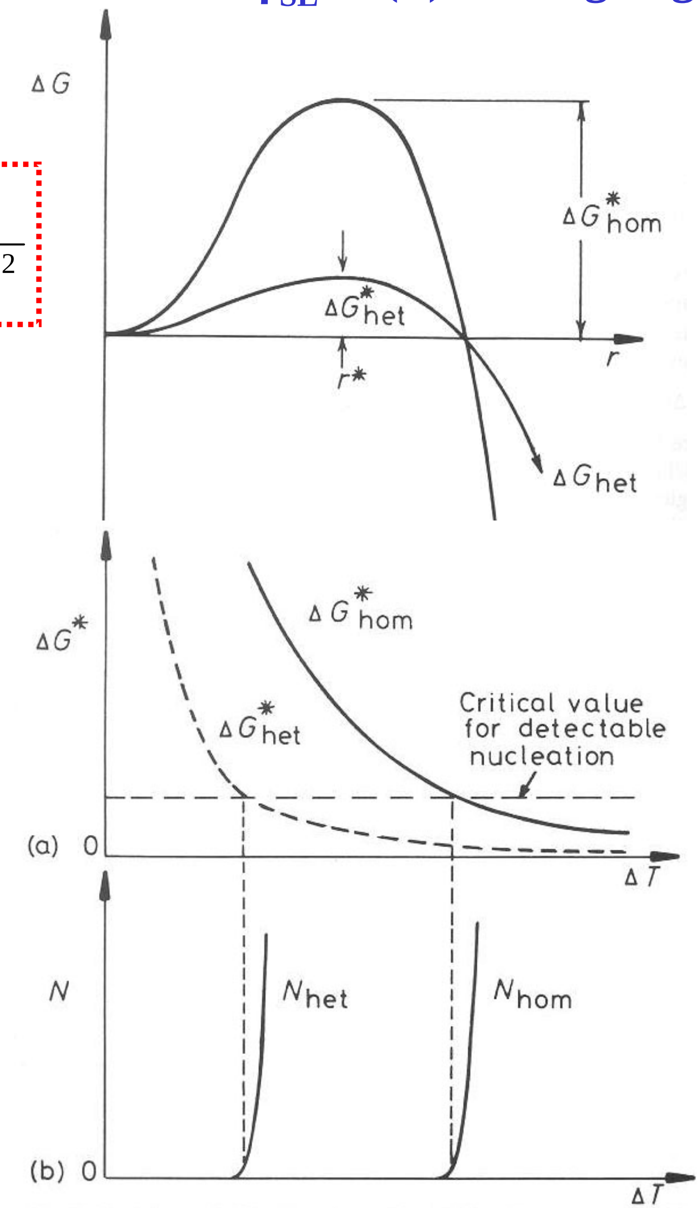
- **Heterogeneous Nucleation**

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

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

- **Nucleation of melting**

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



4.1.4. Nucleation of melting

Although nucleation during solidification usually requires some undercooling, melting invariably occurs at the equilibrium melting temperature even at relatively high rates of heating.

Why?

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

In general, wetting angle = 0 $\Rightarrow$ **No superheating required!**

Contents for today's class

Solidification: Liquid $\longrightarrow$ Solid

< Nucleation >

- Nucleation in Pure Metals
- Homogeneous Nucleation
- Heterogeneous Nucleation
- Nucleation of melting

&

< Growth >

- **Equilibrium Shape and Interface Structure on an Atomic Scale**
- **Growth of a pure solid**

  1) Continuous growth

  : Atomically rough or diffuse interface

  2) Lateral growth

  : Atomically flat of sharply defined interface

- **Heat Flow and Interface Stability**

"Growth"

- **We have learned nucleation.**
  Once nucleated, the nucleus will grow. ➡ **How does it grow?**

- **In order to see the details of growth,**
  we need to know the structure of the surface on an atomic scale.

- **How does it look like?**

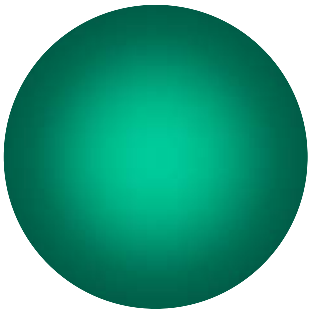
- **Do liquid and solid nuclei differ in growth mechanism?**

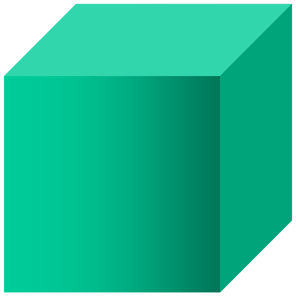
Water Drops ⟺ Natural Minerals

Topaz (황옥)

Stibnite (휘안광)

Equilibrium Shape and Interface Structure on an Atomic Scale





How do you like to call them?

rough interface

singular (smooth) interface

What about the dependence of surface energy on crystal directions?

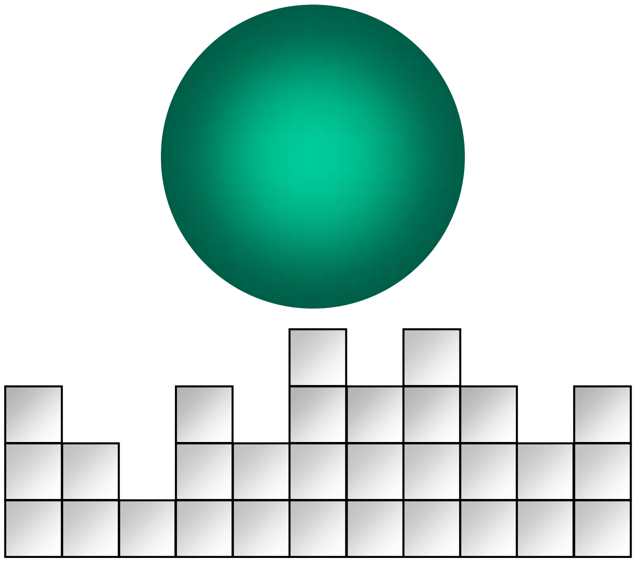
isotropic γ

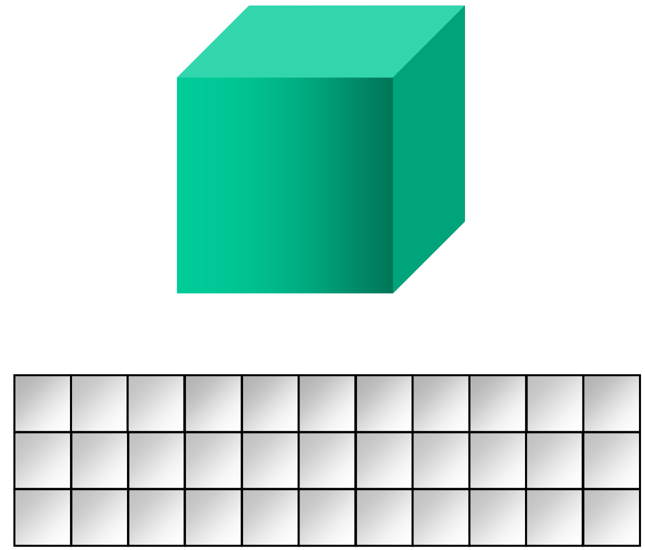
anisotropic γ

Compare the kinetic barrier for atomic attachment.

Which has a low growth barrier?

Equilibrium Shape and Interface Structure on an Atomic Scale





atomically-disordered

atomically-flat

Apply thermodynamics to this fact and derive more information.

Entropy-dominant

weak bonding energy

stable at high T

결정학적 방위에 무관:
γ-plot이 구형임

Enthalpy-dominant

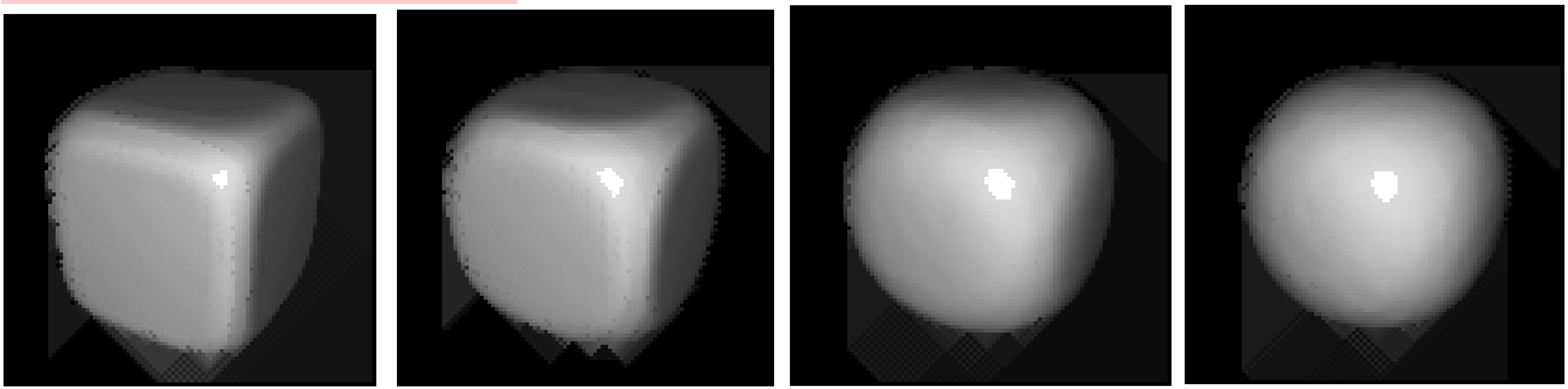
strong bonding energy

stable at low T

결정학적 이방성 효과:
낮은 지수 갖는 조밀면으로 둘러싸인 형상

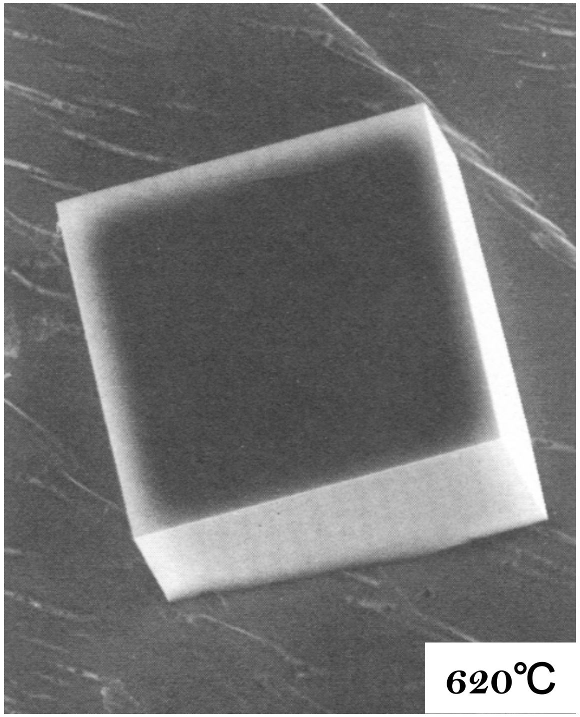
Thermal Roughening

singular (smooth) interface **rough interface**

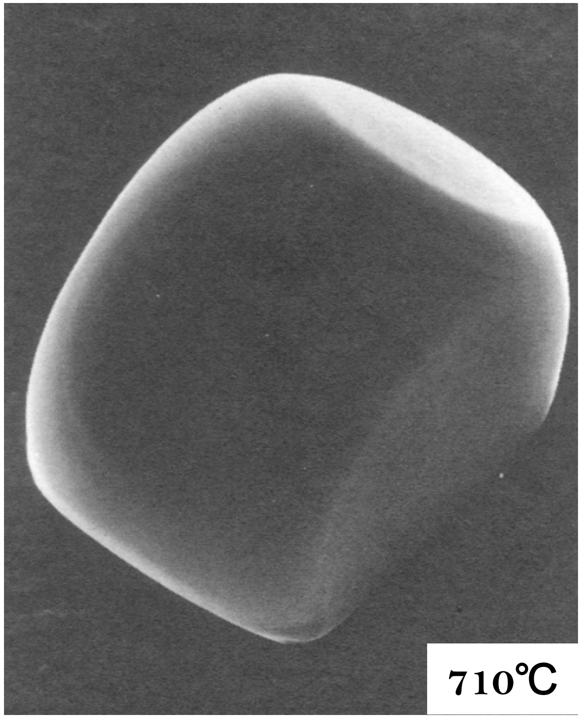


Heating up to the roughening transition.

✓ Equilibrium shape of NaCl crystal



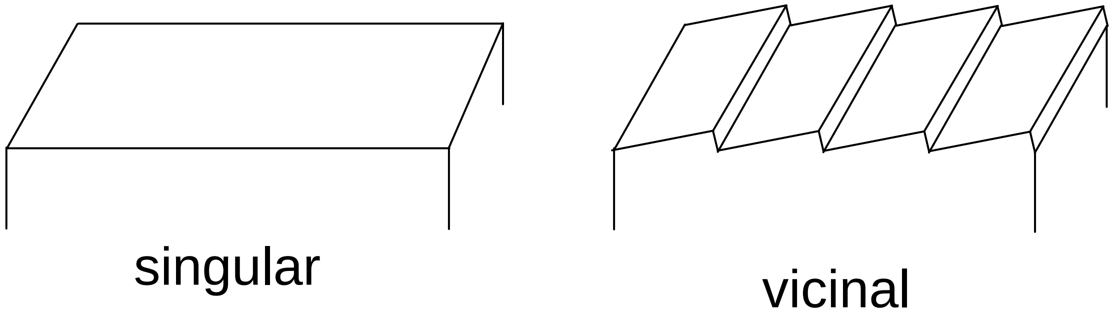
Thermal Roughening



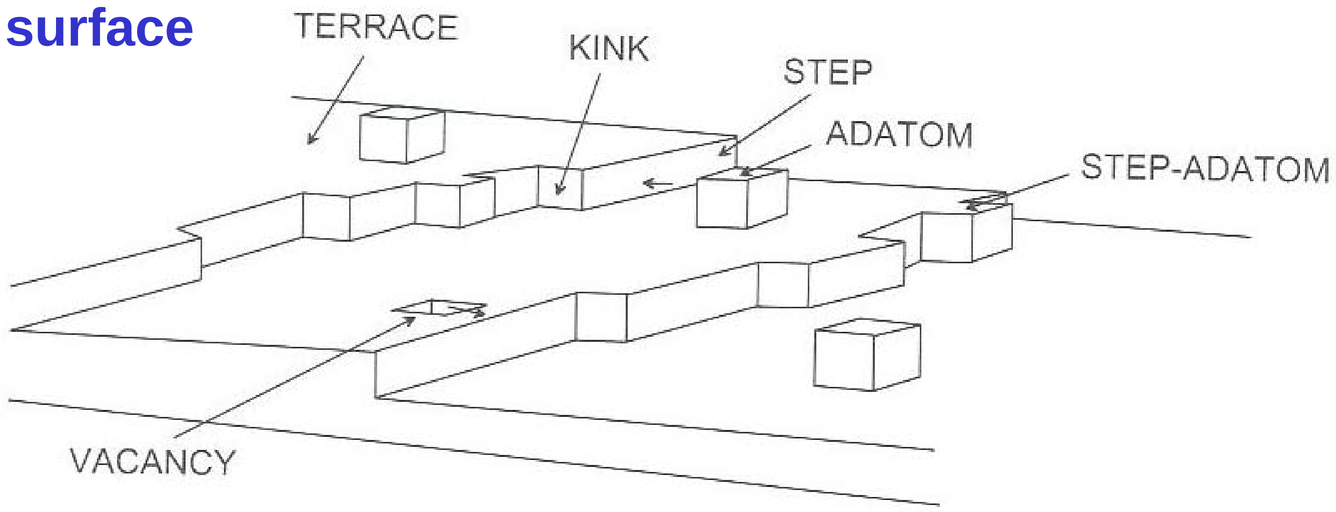
J.C. Heyraud, J.J. Metois, J. Crystal Growth , 84, 503 (1987)

Atomic View

Ideal Surfaces



More realistic surface

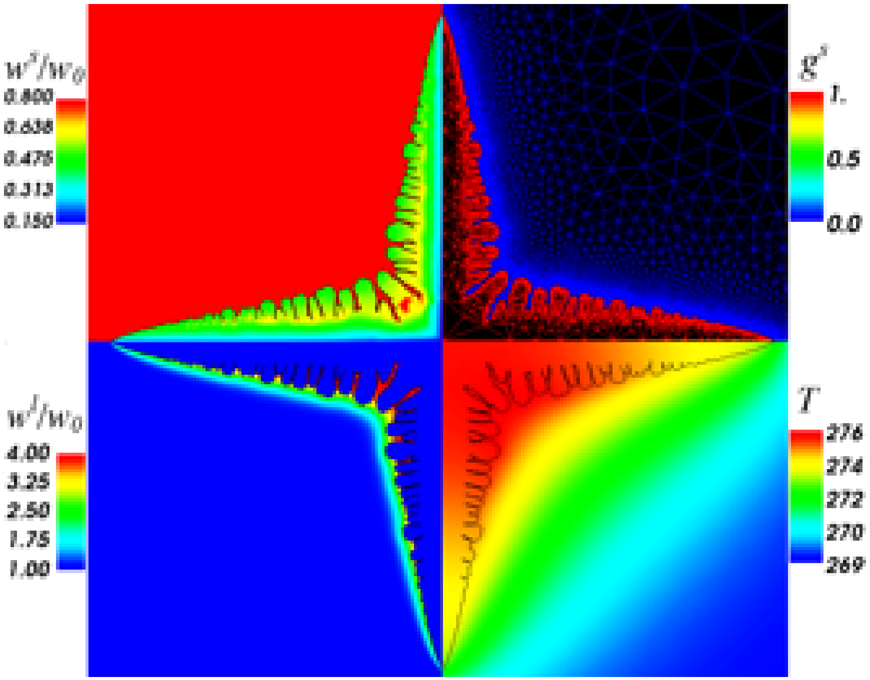


- Realistic surfaces of crystals typically look like this at low temperature
- At sufficiently high temperature, the structure becomes atomically rough

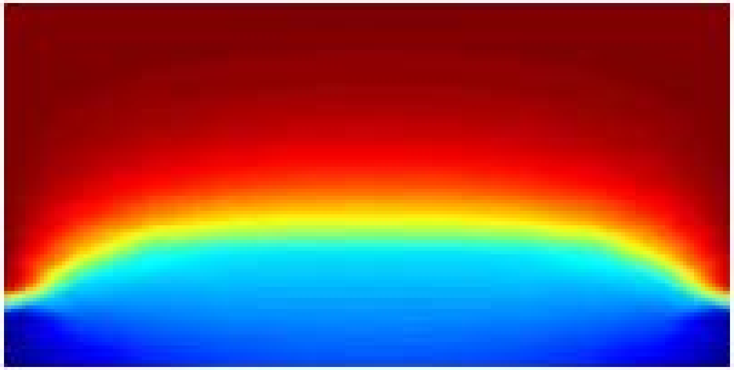
4.2. Growth of a pure solid

Two types of solid-liquid interface

1. **Continuous growth**
   : Atomically rough or diffuse interface

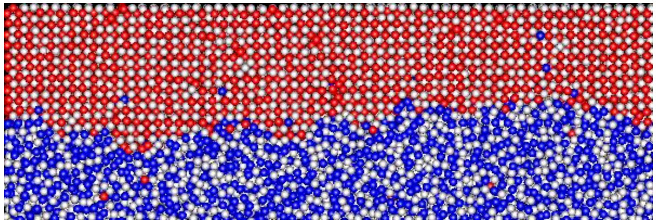


2. **Lateral growth**
   : Atomically flat of sharply defined interface



4.2.1 Continuous growth

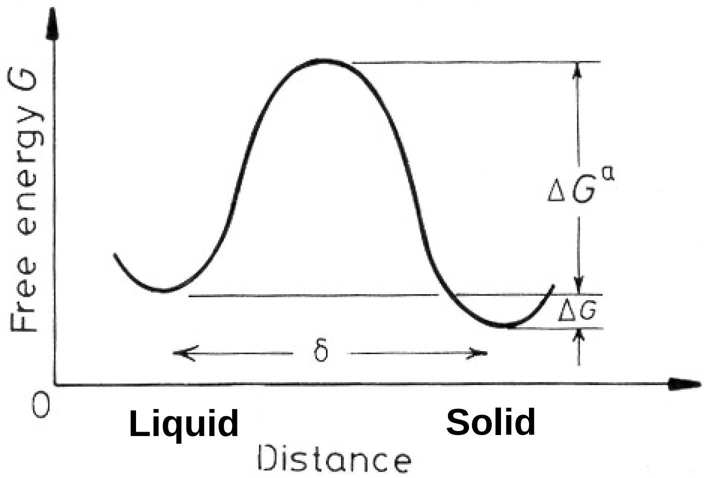
The migration of a rough solid/liquid interface can be treated in a similar way to the migration of a random high angle grain boundary.



- Driving force for solidification

$$\boxed{\Delta G = \frac{L}{T_m}\Delta T_i}$$

$\boldsymbol{L}$: latent heat of melting
$\Delta \boldsymbol{T}_i$: undercooling of the interface



- Net rate of solidification

$$\boxed{v = k_1 \Delta T_i}$$

$\boldsymbol{k_1}$: properties of boundary mobility

Reference (eq. 3.21) $v = M \cdot \Delta G / V_m$

The solidification of metals is usually a diffusion controlled process.

- **Pure metal grow at a rate controlled by heat conduction.**
- **Alloy grow at a rate controlled by solute diffusion.**

4.2.2 Lateral growth

- **Materials with a high entropy of melting prefer to form atomically smooth, closed-packed interfaces.**
- **For this type of interface the minimum free energy also corresponds to the minimum internal energy, i.e. a minimum number of broken 'solid' bonds.**

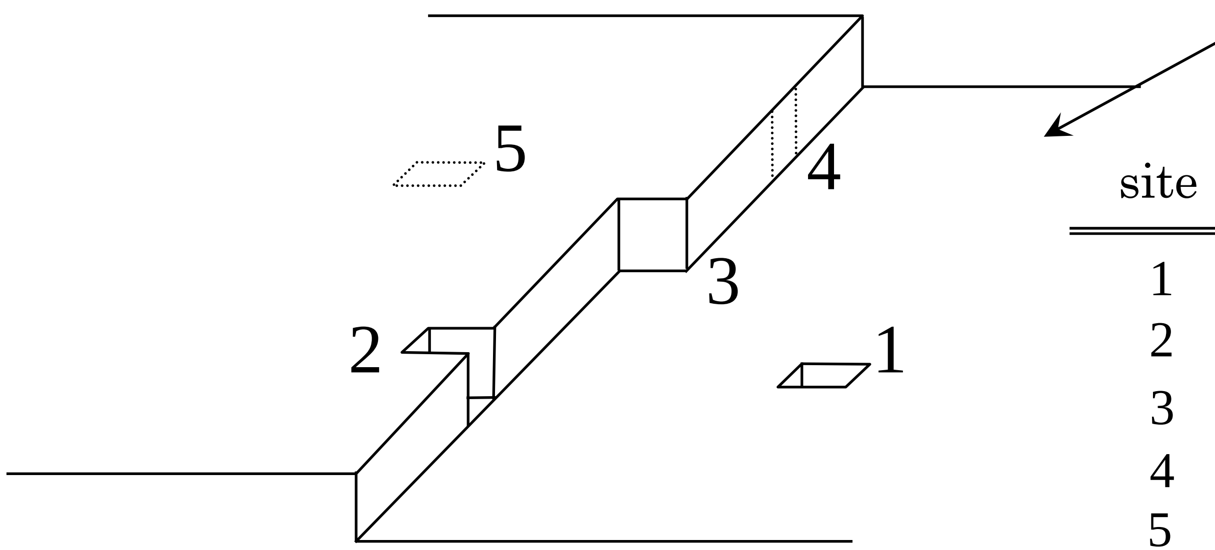
Two ways in which ledges and jogs (kinks) can be provided.

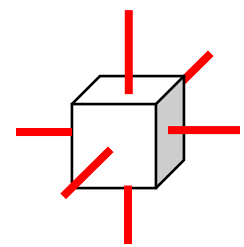
1) Surface (2-D) nucleation

2) Spiral growth

Condition for Atomic Attachment

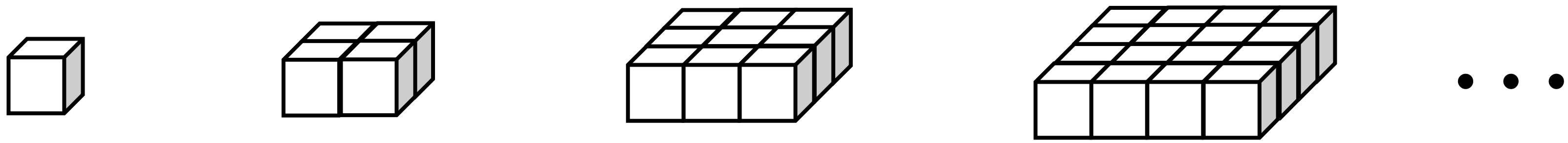
Suppose the building unit (atom) has 6 bonds to be saturated





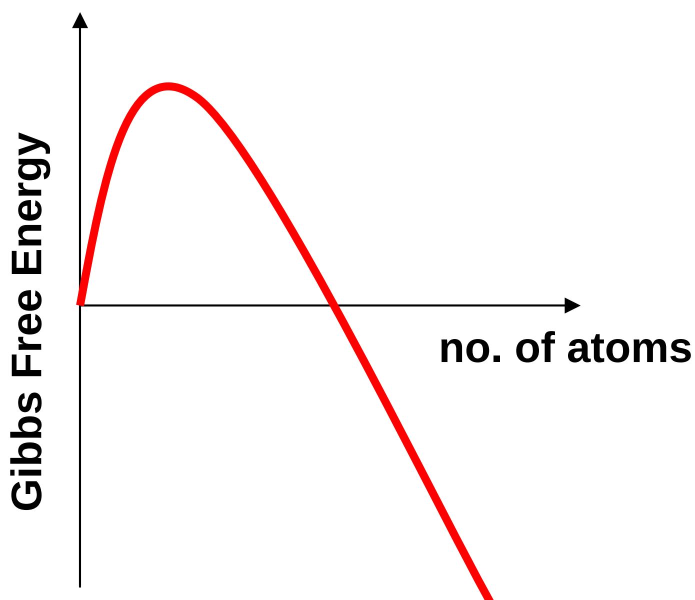
site	ΔE / *atom*		
1	-4ϕ	*stable*	
2	-2ϕ	*stable*	
3	0ϕ	*stable*	: *kink*
4	$+2\phi$	*unstable*	
5	$+4\phi$	*unstable*	

How many unsaturated bonds are there if they are epitaxial to the underneath atomic layer?



$+4\phi/atom$	$+8\phi/4\ atoms$	$+12\phi/9\ atoms$	$+16\phi/16\ atoms$
$\Delta f = -kT\ln(P/P_e)$	$2\Delta f$	$9\Delta f$	$16\Delta f$
$+4\phi/atom$	$+2\phi/atom$	$+\frac{4}{3}\phi/atom$	$+1\phi/atom$
Δf	Δf	Δf	Δf

Draw the plot showing how the free energy varies with the number of atoms in the presence of supersaturation (driving force) for growth.



→ 2- Dimensional Nucleation

- **if large # of atoms → form a disc-shaped layer,**
- **self-stabilized and continue to grow.**
- **ΔT becomes large, r* ↓.**
- $v \propto \exp(-k^2/\Delta T_i)$

2) Spiral growth: Growth by Screw Dislocation

Crystals grown with a low supersaturation were always found to have a 'growth spirals' on the growing surfaces.

- **addition of atoms to the ledge cause it to rotate around the axis of screw dislocation**
- **If atoms add at an equal rate to all points along the step, the angular velocity of the step will be initially greatest nearest to the dislocation core.**
- **the spiral tightens until it reaches a min radius of r***
- **v (growth rate) = $k_3(\Delta T_i)^2$**

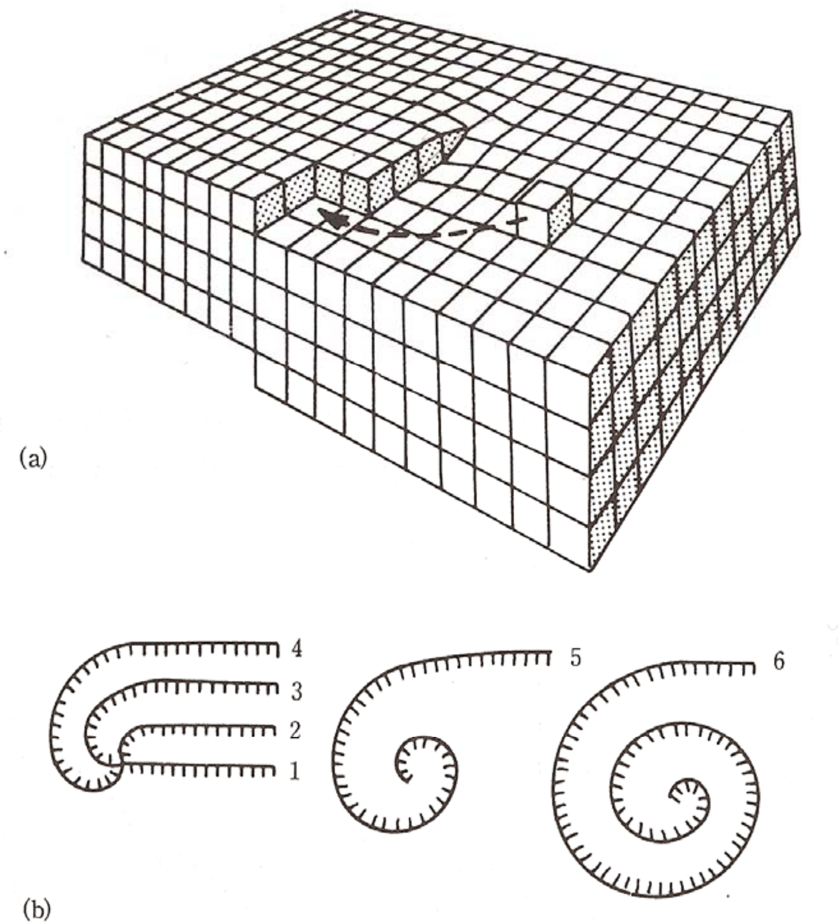
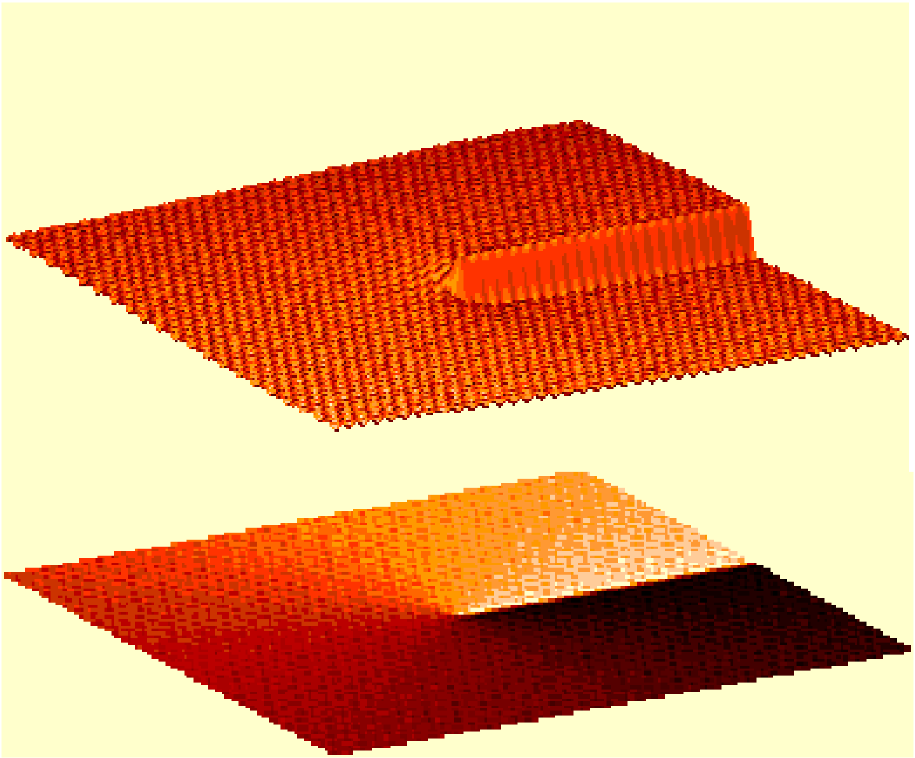


그림 4.13 나선형 성장 (b) 나선전위가 표면과 만나면 표면에는 돌출맥이 생김 (b) 원자가 이 돌출맥에 붙을 때 이 돌출맥은 면상에서 회전을 하며 회전속도는 전위로부터 멀어질수록 감소함.

Growth by Screw Dislocation



Burton, Cabrera and Frank (BCF, 1948) elaborated the spiral growth mechanism, assuming steps are atomically disordered...

Their interpretation successfully explained the growth velocity of crystals as long as the assumption is valid…

3) Growth from twin boundary

- **another permanent source of steps like spiral growth**

  → not monoatomic height ledge but macro ledge

Kinetic Roughening

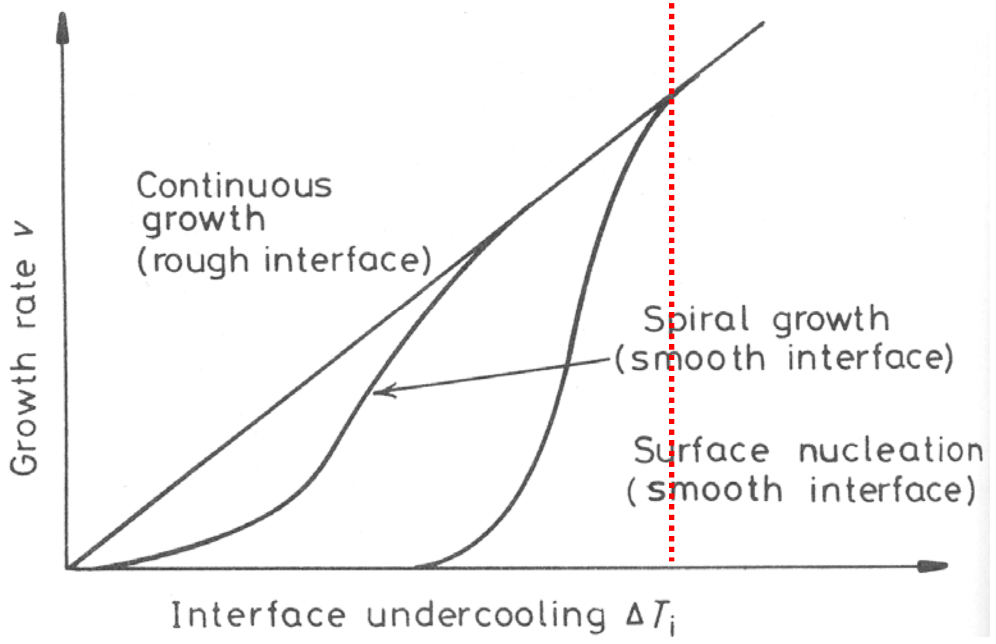
Rough interface **- Ideal Growth → diffusion-controlled → dendritic growth**

Singular interface - **Growth by Screw Dislocation**
Growth by 2-D Nucleation

The growth rate of the singular interface cannot be higher than ideal growth rate.

When the growth rate of the singular Interface is high enough, it follows the ideal growth rate like a rough interface.

→ kinetic roughening

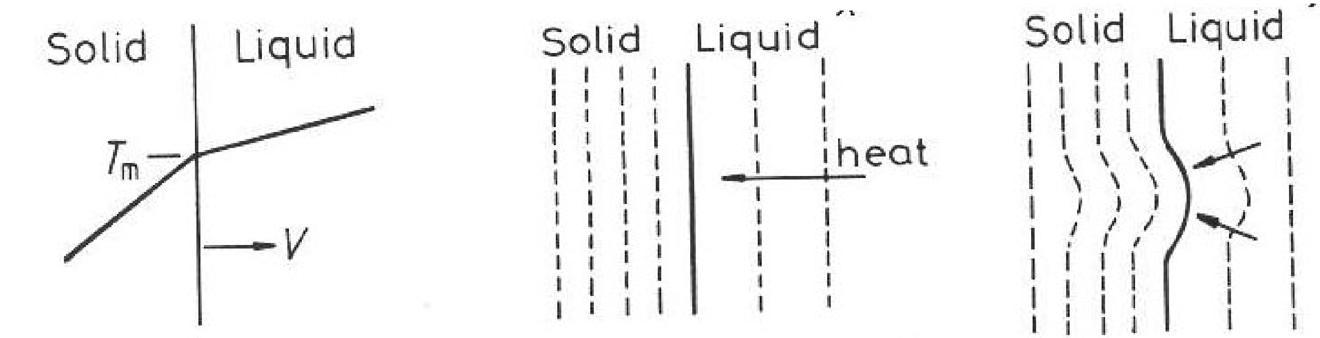


4.2.3 Heat Flow and Interface Stability - Planar interface

1) Superheated liquid

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 $K_S T'$

$K_L T'_L$ **- 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)

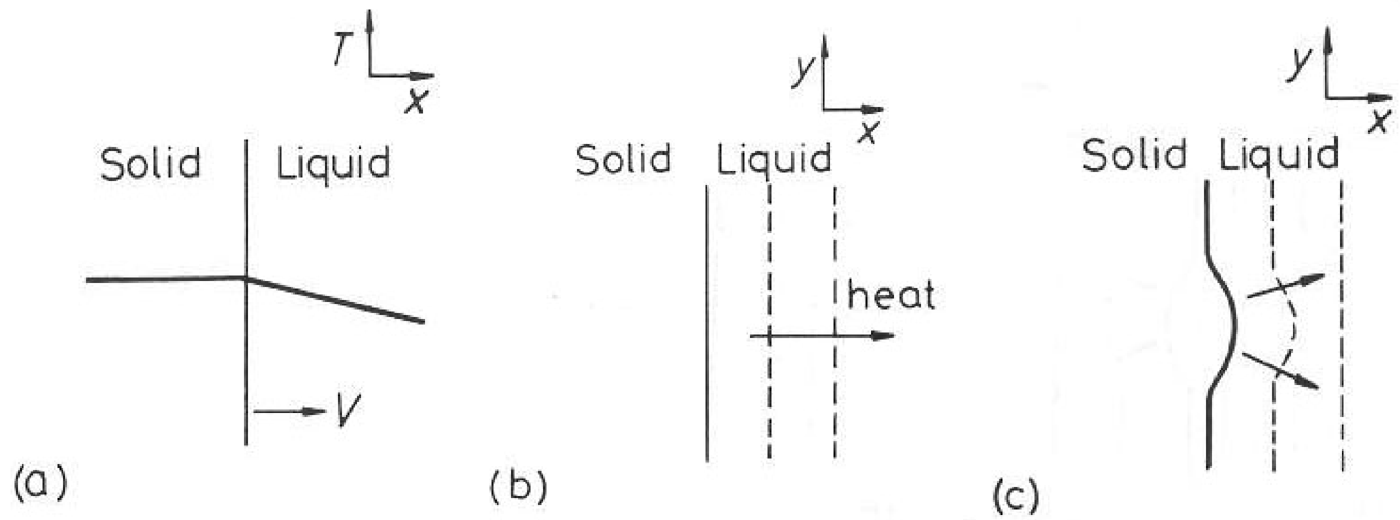
dT/dx in the liquid ahead of the protrusion will increase more positively. **T_L'↑ & T_S'↓**

More heat to the protrusion → melt away
v of protrusion ↓ to match other v in planar region

mould walls

4.2.3 Heat Flow and Interface Stability - Planar interface

2) Solid growing into supercooled liquid



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

- heat flow from solid = the protrusion grows preferentially.

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**

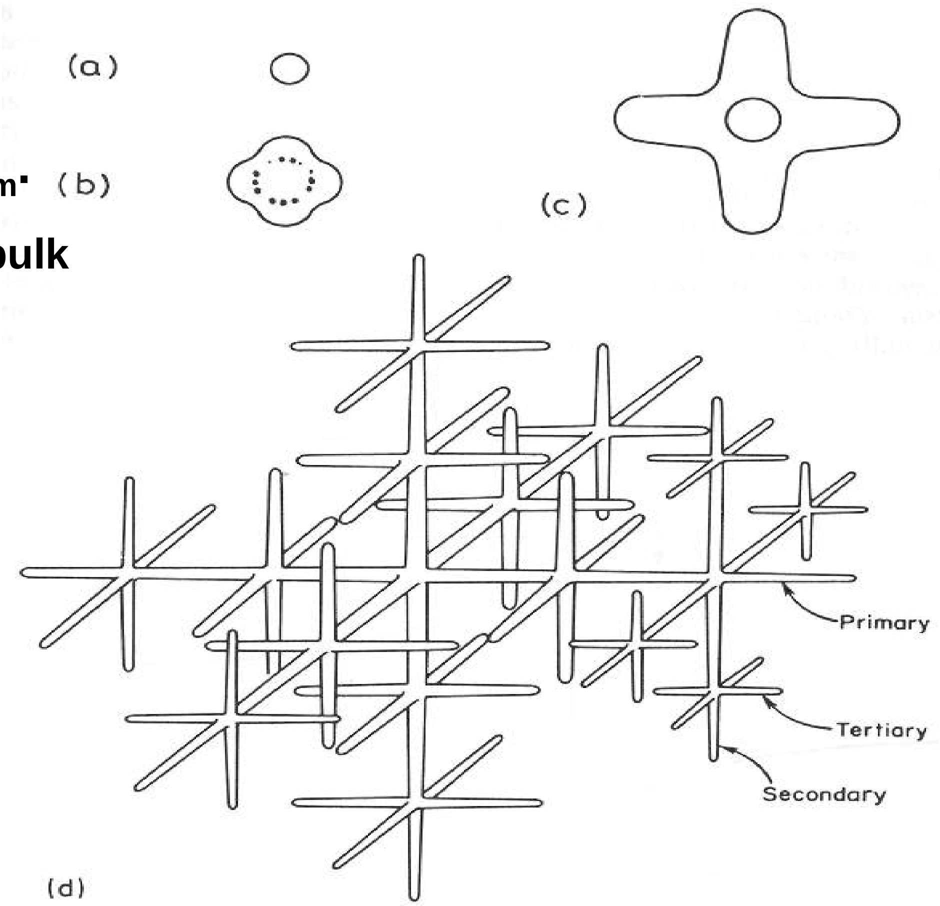
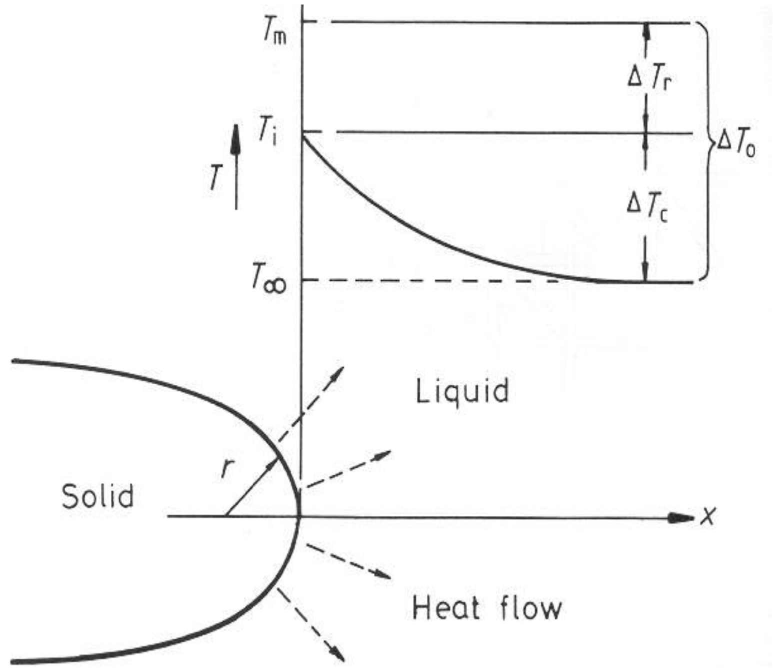


Fig. 4.17 The development of thermal dendrites: (a) a spherical nucleus; (b) the interface becomes unstable; (c) primary arms develop in crystallographic directions (<100> in cubic crystals); (d) secondary and tertiary arms develop

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 $K_S T_S' = K_L T_L' + vL_V$

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

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 also depends on r. How?

Thermodynamics at the tip?

Gibbs-Thomson effect:
melting point depression

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

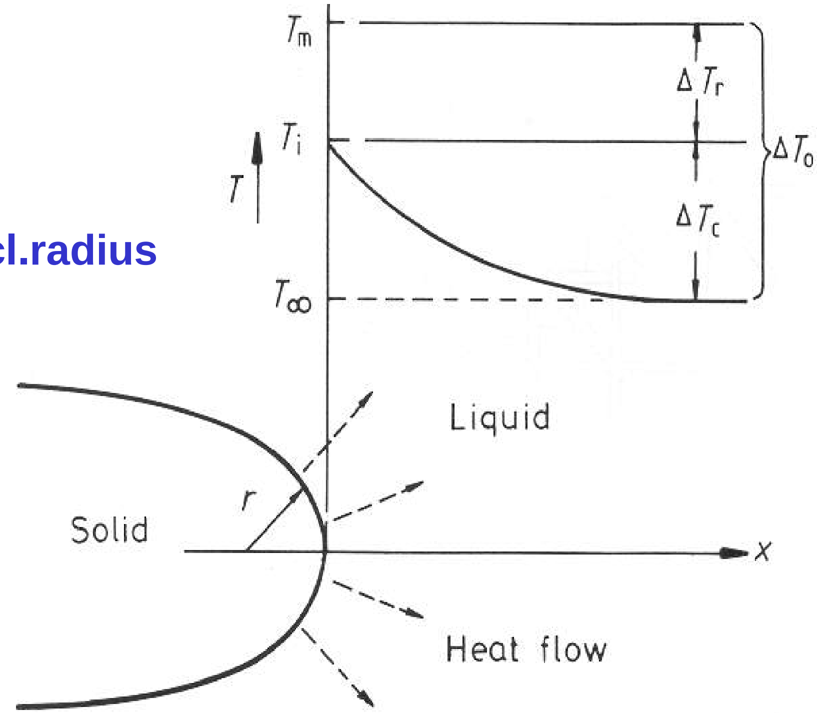
Minimum possible radius (r)?

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

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.

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

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

$v \rightarrow 0 \;\; as\; r \rightarrow r^* \;\; due\; to\; Gibbs\text{-}Thomson\; effect$

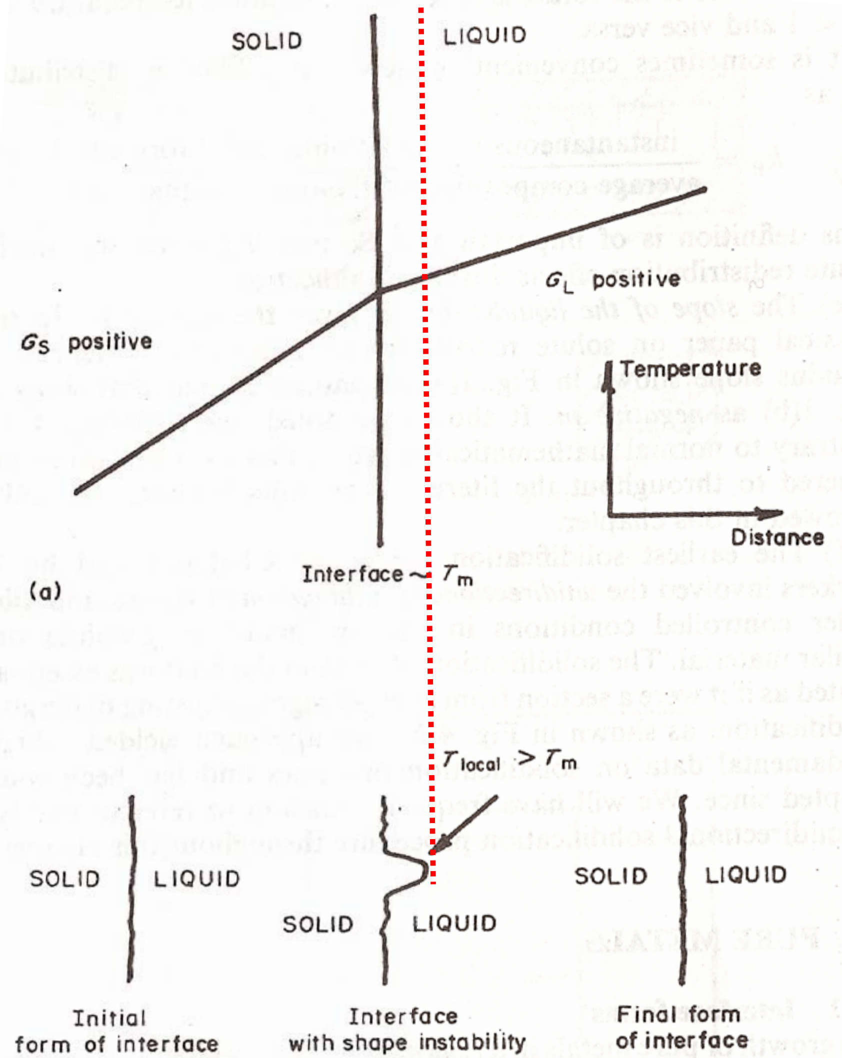
$as\; r \rightarrow \infty \;\; due\; to\; slower\; heat\; condution$

Maximum velocity?

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

Heat Flow and Interface Stability - Planar interface

1) Superheated liquid



2) Supercooled liquid