2018 Fall

"Phase Transformation *in* Materials"

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Contents for today's class

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 ↑

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

- Heterogeneous Nucleation

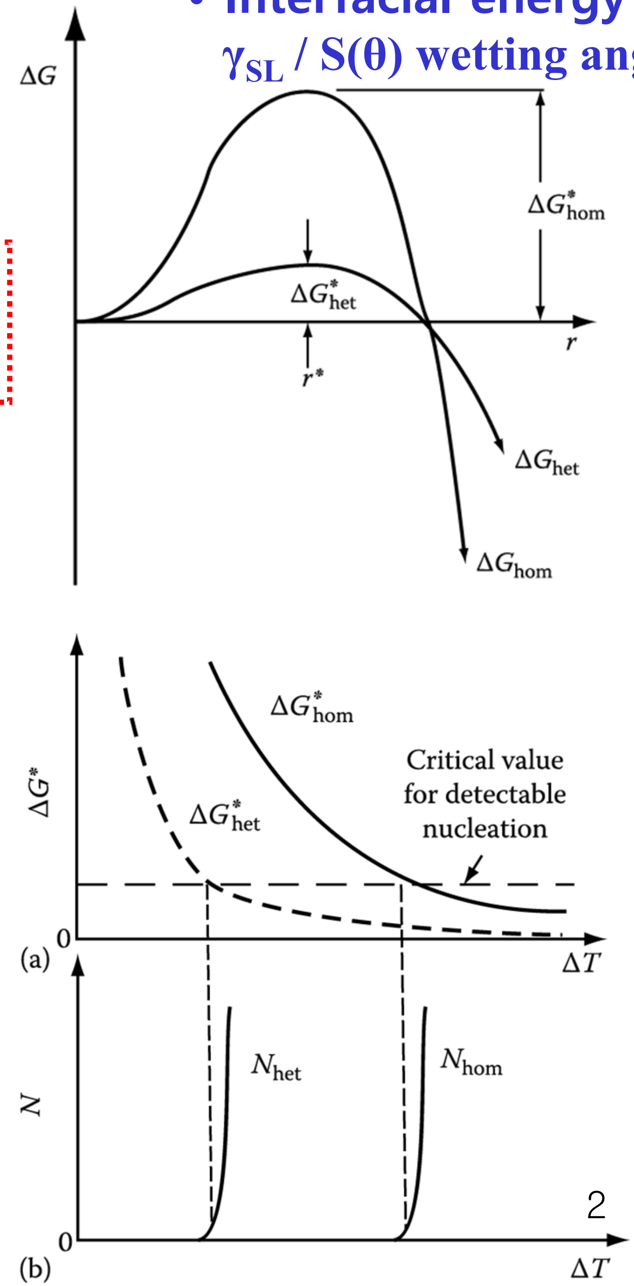
$$\Delta G^*_{het} = S(\theta)\Delta G^*_{hom}$$

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

- Nucleation of melting

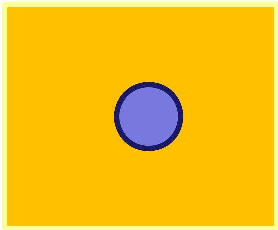
$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$ **(commonly)**

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



Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

Liquid | T_m | Undercooled Liquid | Solid

No superheating required!

- Interfacial energy ⇨ No ΔT_N

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

Melting: Liquid ← Solid

Solidification: Liquid → Solid

< Nucleation >
&
< Growth >

• Nucleation in Pure Metals

• 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

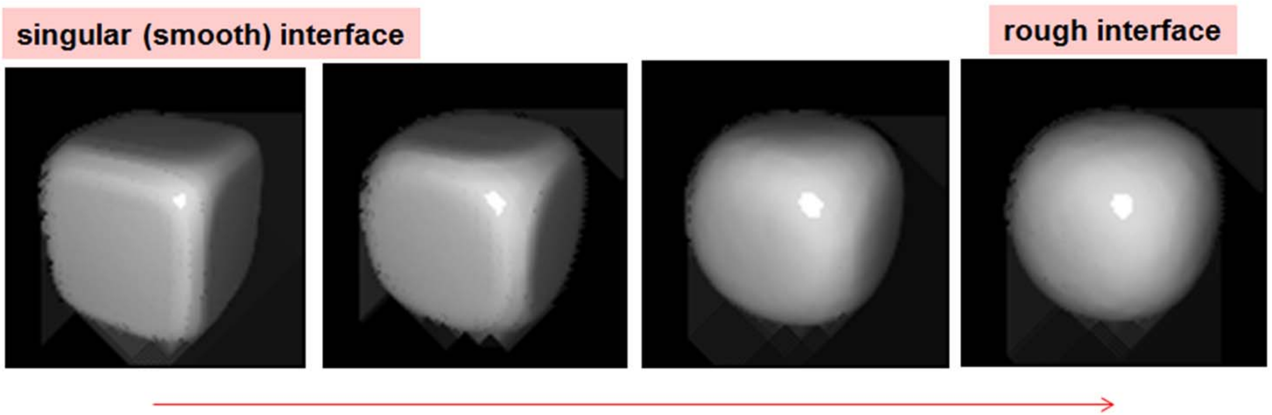
• Heat Flow and Interface Stability

4.3 Alloy solidification

- Solidification of single-phase alloys
- Eutectic solidification
- Off-eutectic alloys
- Peritectic solidification

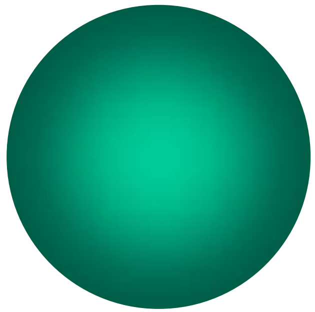
Q: Rough interface vs Singular interface?

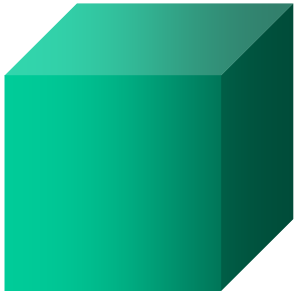
Thermal Roughening



Heating up to the roughening transition.

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?

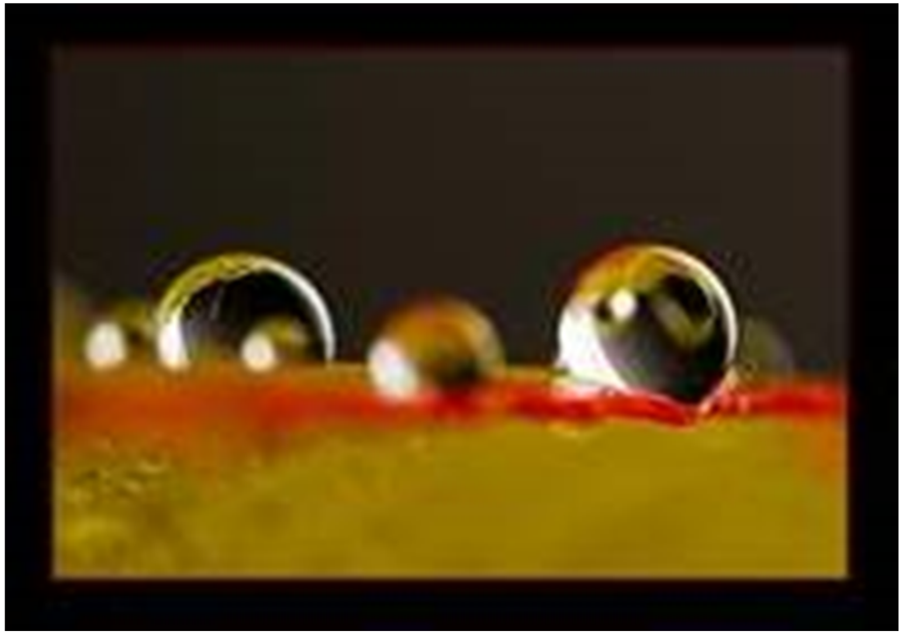
isotropic γ

Do not vary with crystallographic orientation,
i.e, γ-plots are spherical

anisotropic γ

Strong crystallographic effects,
: solidify with low-index close-packed facets

Water Drops ⟷ Natural Minerals

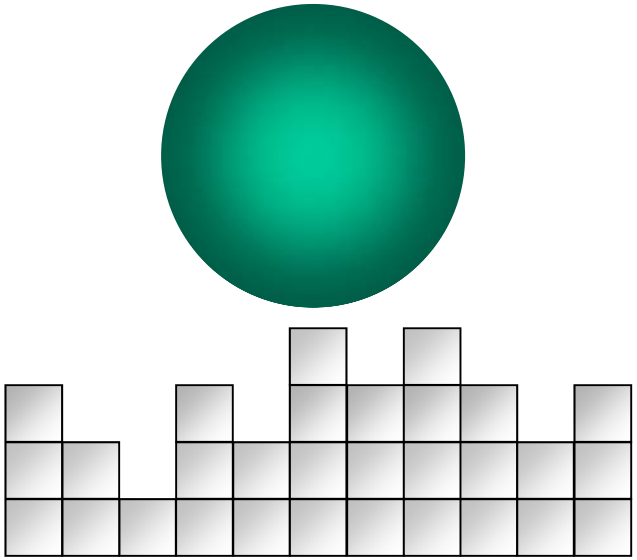


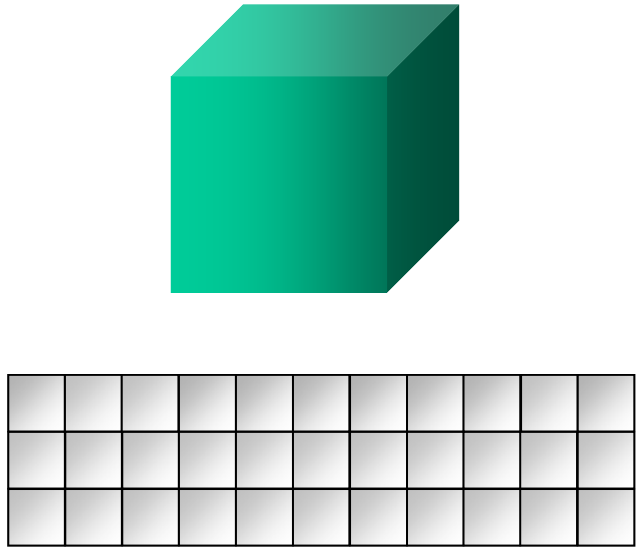
Topaz (황옥)

Stibnite (휘안광)

How differ the structure of the surface on an atomic scale?

Equilibrium Shape and Interface Structure on an Atomic Scale





atomically-disordered

Ex) metallic systems

atomically-flat

nonmetals

Apply thermodynamics to this fact and derive more information.

stable at high T

stable at low T

Entropy-dominant

Enthalpy-dominant

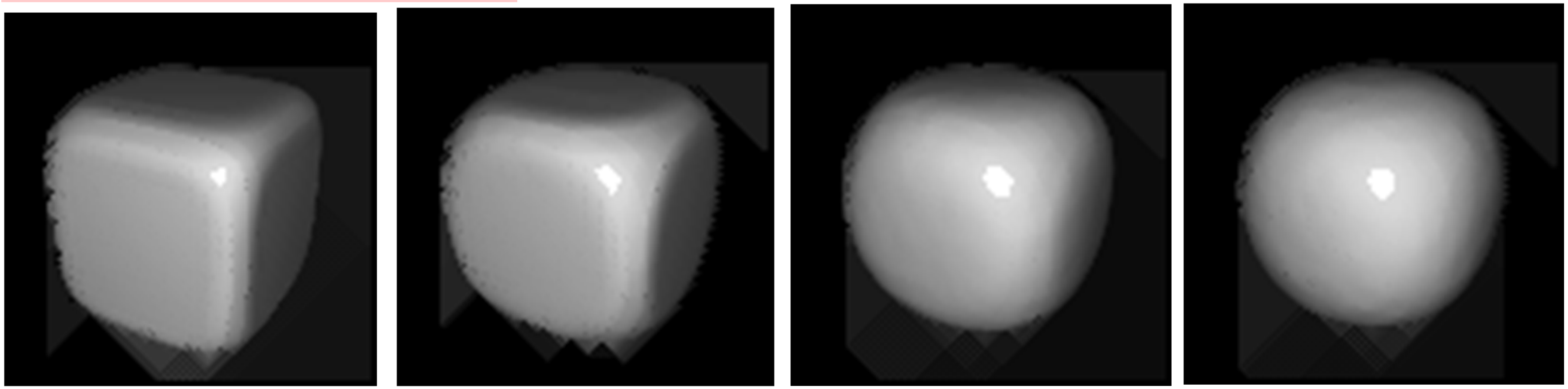
weak bonding energy

strong bonding energy

Thermal Roughening

singular (smooth) interface

rough interface



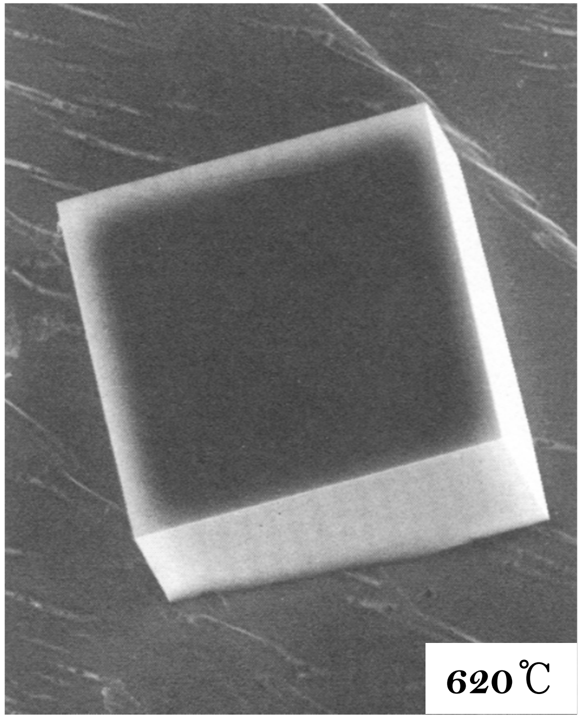
Enthalpy-dominant

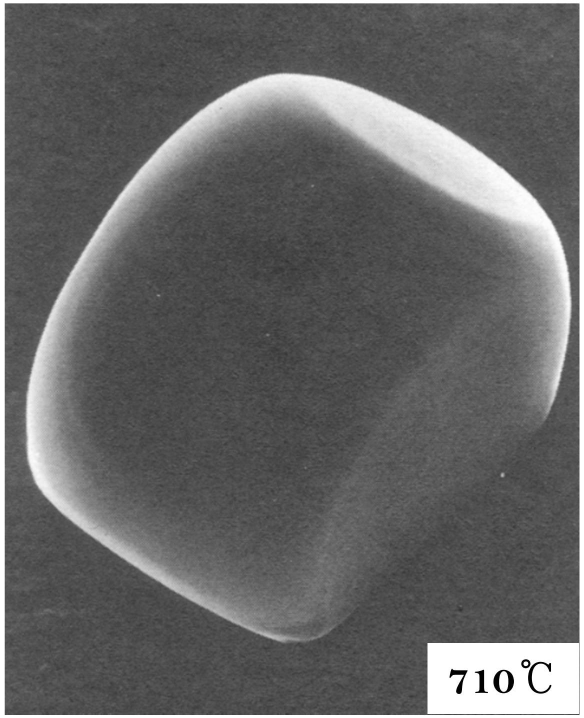
Entropy-dominant

Heating up to the roughening transition.

✓ Equilibrium shape of NaCl crystal

Thermal Roughening





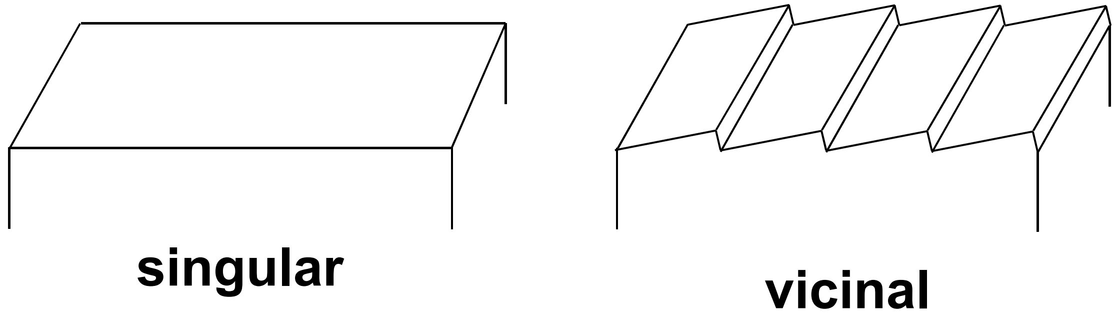
J.C. Heyraud, J.J. Metois, J. Crystal Growth , 84, 503 (1987)

Compare the kinetic barrier for atomic attachment.

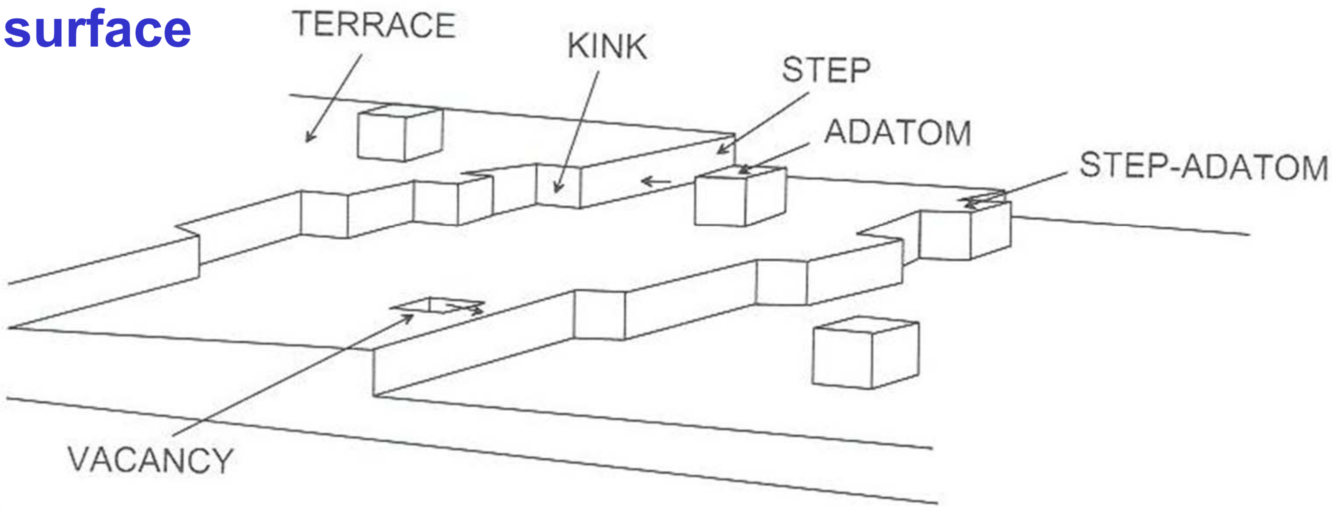
Which has a low growth barrier?

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**

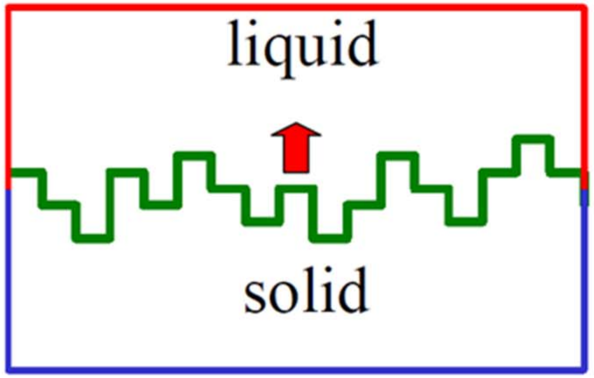
(Thermal Roughening)

Q: What kinds of Growth in a pure solid exist?

Two types of solid-liquid interface

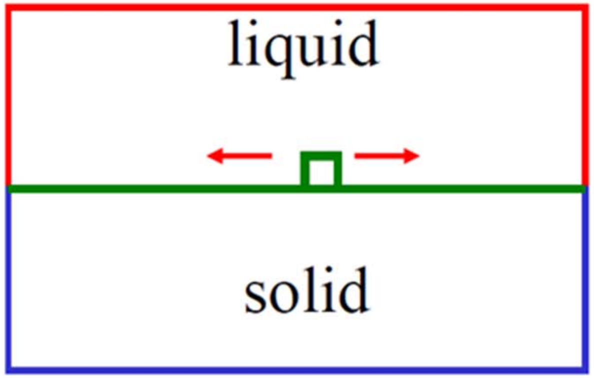
a) Continuous growth

: Atomically rough or diffuse interface



b) Lateral growth

: Atomically flat of sharply defined interface



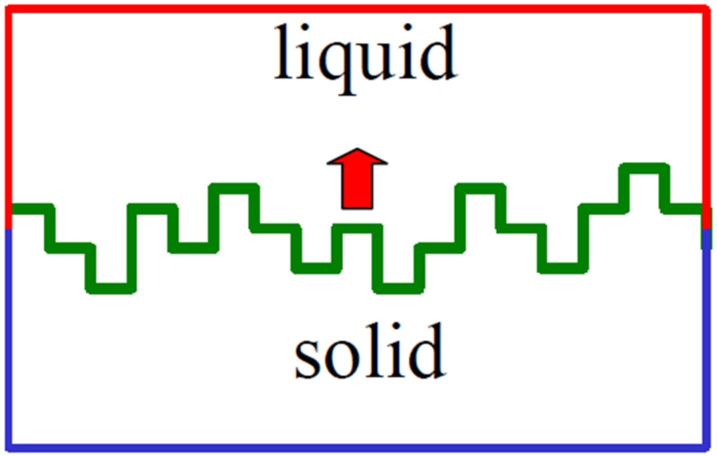
4.2. Growth of a pure solid

: The next step after the nucleation is growth.

Two types of solid-liquid interface

a) Continuous growth

: Atomically rough or diffuse interface



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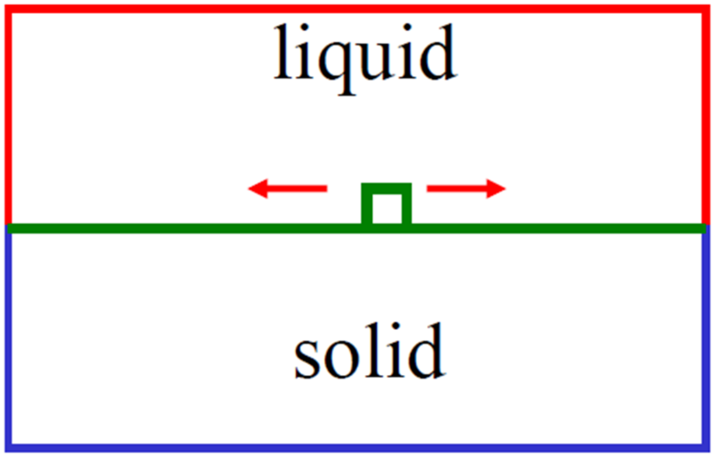

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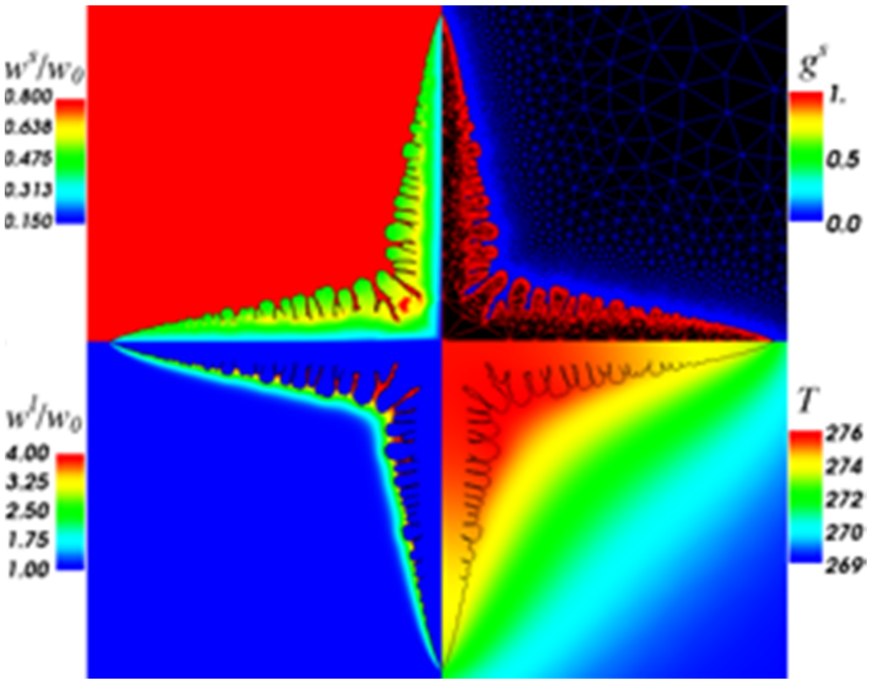

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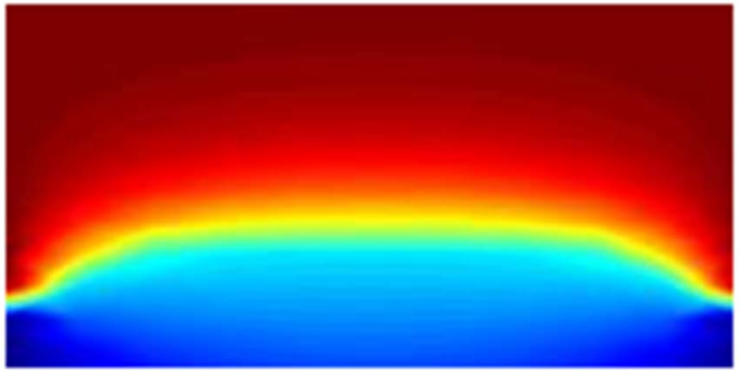
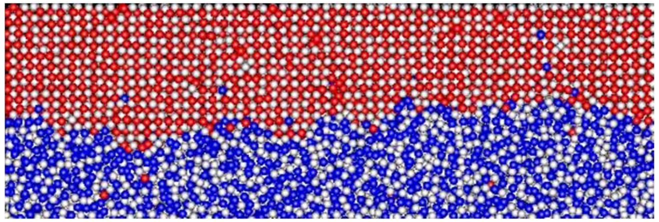


a) Continuous growth

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.

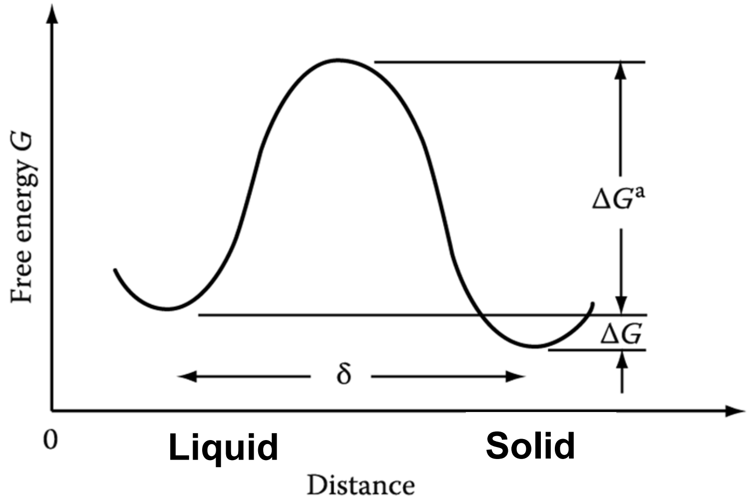


- Driving force for solidification

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

L: latent heat of melting

ΔT_i : undercooling of the interface



- Net rate of solidification

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

k_1: properties of boundary mobility

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

The rate of the continuous growth (typical for metals) is usually a "diffusion controlled process".

Pure metal grow at a rate controlled by heat transfer to the interfacial region.

Alloy grow at a rate controlled by solute diffusion.

b) Lateral growth

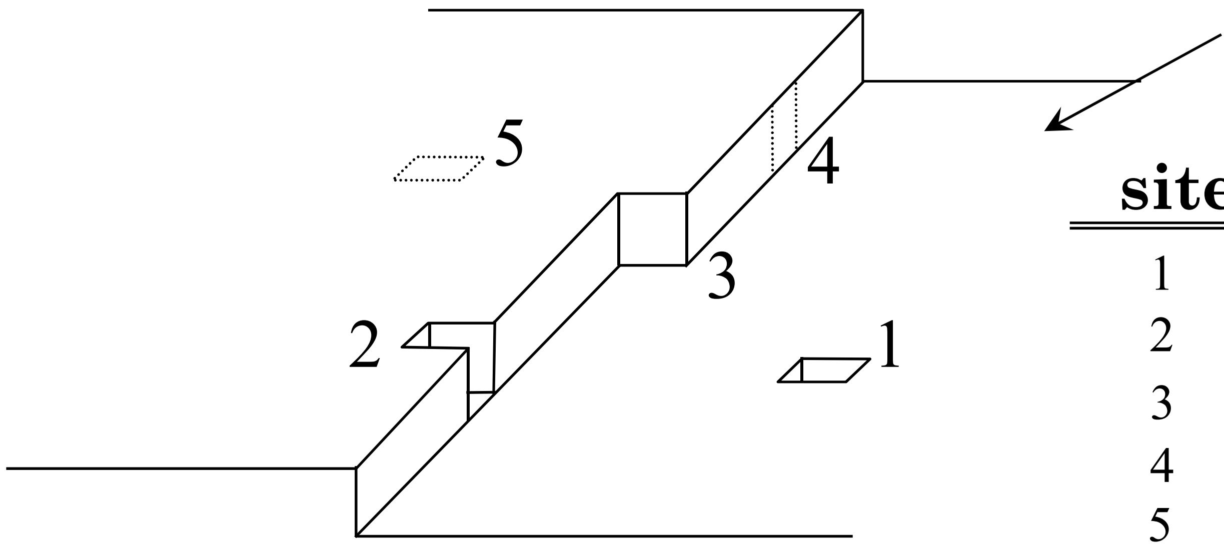
- Materials with a high entropy of melting (~high T_m) prefer to form atomically smooth, closed-packed interfaces.
- For this type of interface the minimum free energy also corresponds to the minimum internal energy, i.e. a minimum number of broken 'solid' bonds.

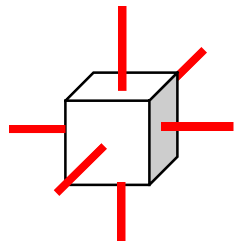
Two ways in which ledges and jogs (kinks) can be provided.

① Surface (2-D) nucleation　　② Spiral growth

Condition for Atomic Attachment

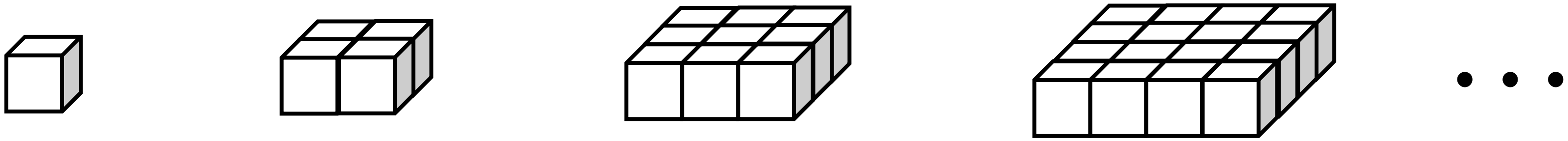
Suppose the building unit (atom) has
6 bonds to be saturated





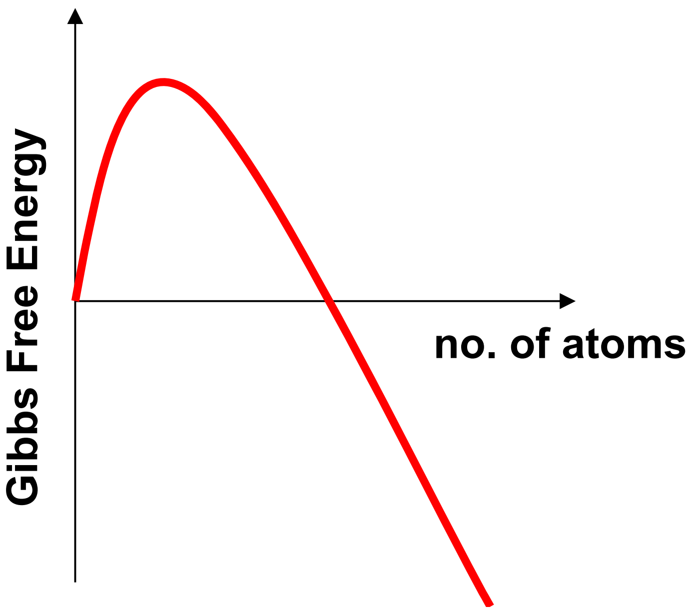
site	ΔE / atom			
1	-4ϕ	stable		
2	-2ϕ	stable		
3	0ϕ	stable	:	kink
4	$+2\phi$	unstable		
5	$+4\phi$	unstable		

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



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

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 ①

- **If large # of atoms form a disc-shaped layer,**

→ self-stabilized and continue to grow.

- **ΔT becomes large, r* ↓.**

- $\boxed{v \propto \exp(-k_2/\Delta T_i)}$

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 minimum radius of r***
- $\boxed{v = k_3(\Delta T_i)^2}$

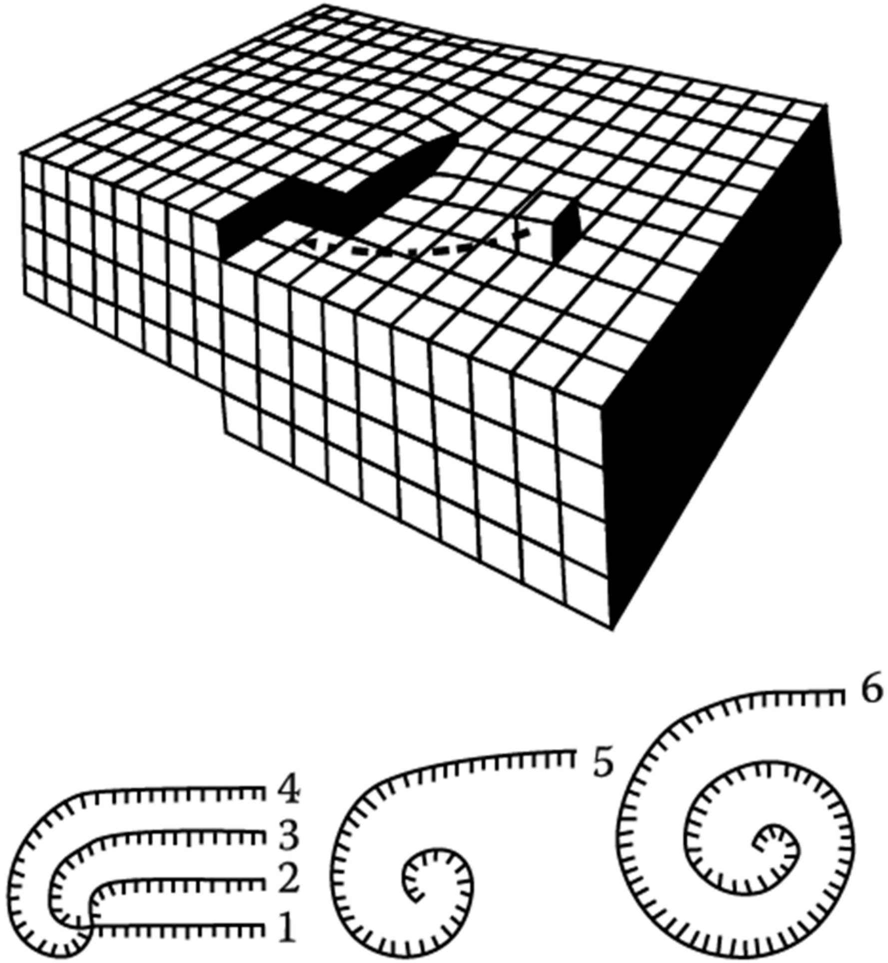
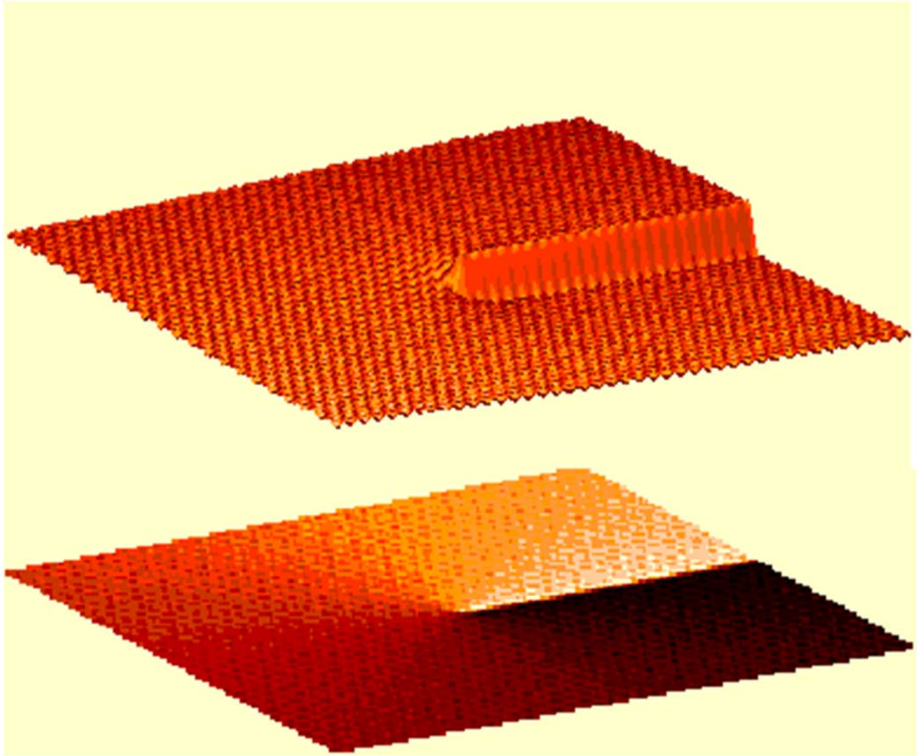


Fig. 4. 13 Spiral growth. (a) A screw dislocation terminating in the solid/liquid interface showing the associated ledge. Addition of atoms at the ledge causes it to rotate with an angular velocity decreasing away from the dislocation core so that a growth spiral develops as shown in (b).

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 → "feather crystal" under small ΔT

- 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

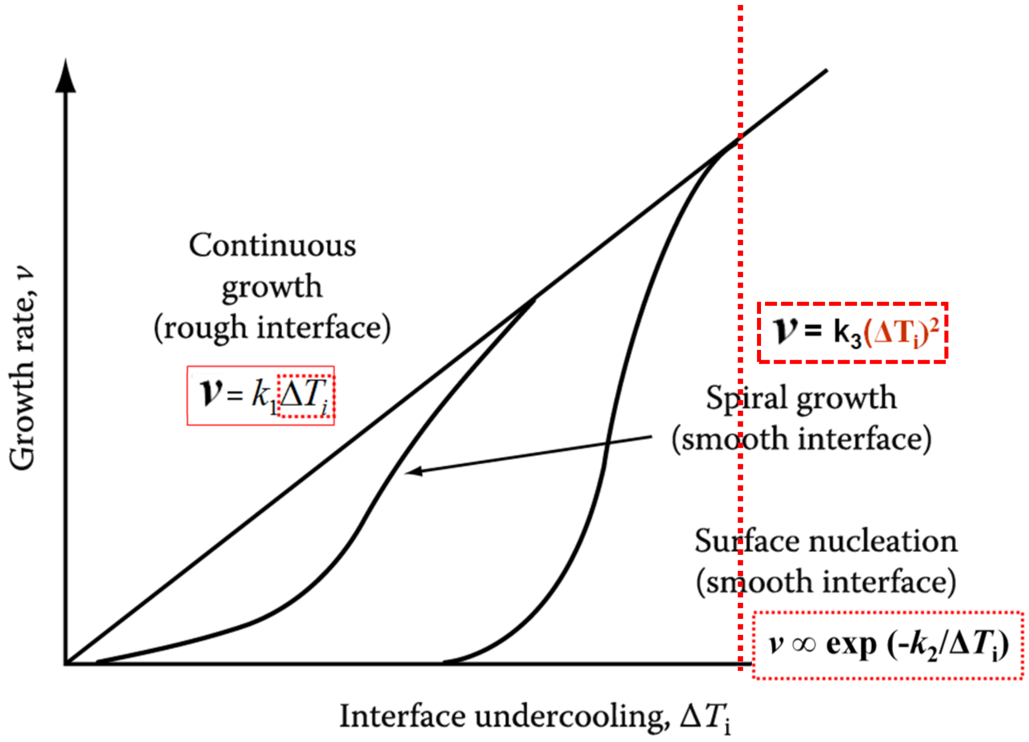
Smooth interface - Growth by Screw Dislocation
Growth by 2-D Nucleation

Small ΔT → "feather" type of growth ⟺ Large ΔT → cellular/dendritic growth

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



Q: Heat Flow and Interface Stability

1) Superheated liquid

: Extraction of latent heat by conduction in the crystal

2) Supercooled liquid

: conduction of latent heat into the liquid

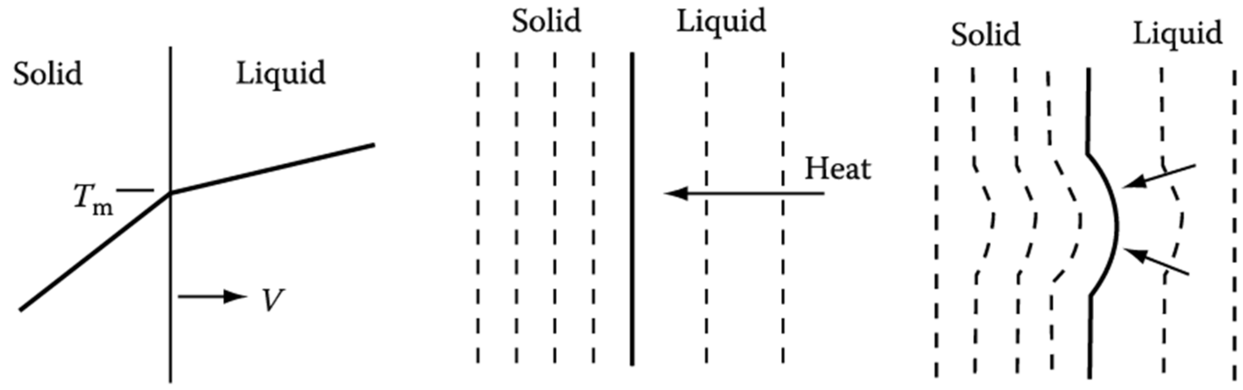
→ Development of Thermal Dendrite

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. $T_L' \uparrow$ & $T_S' \downarrow$

More heat to the protrusion → melt away

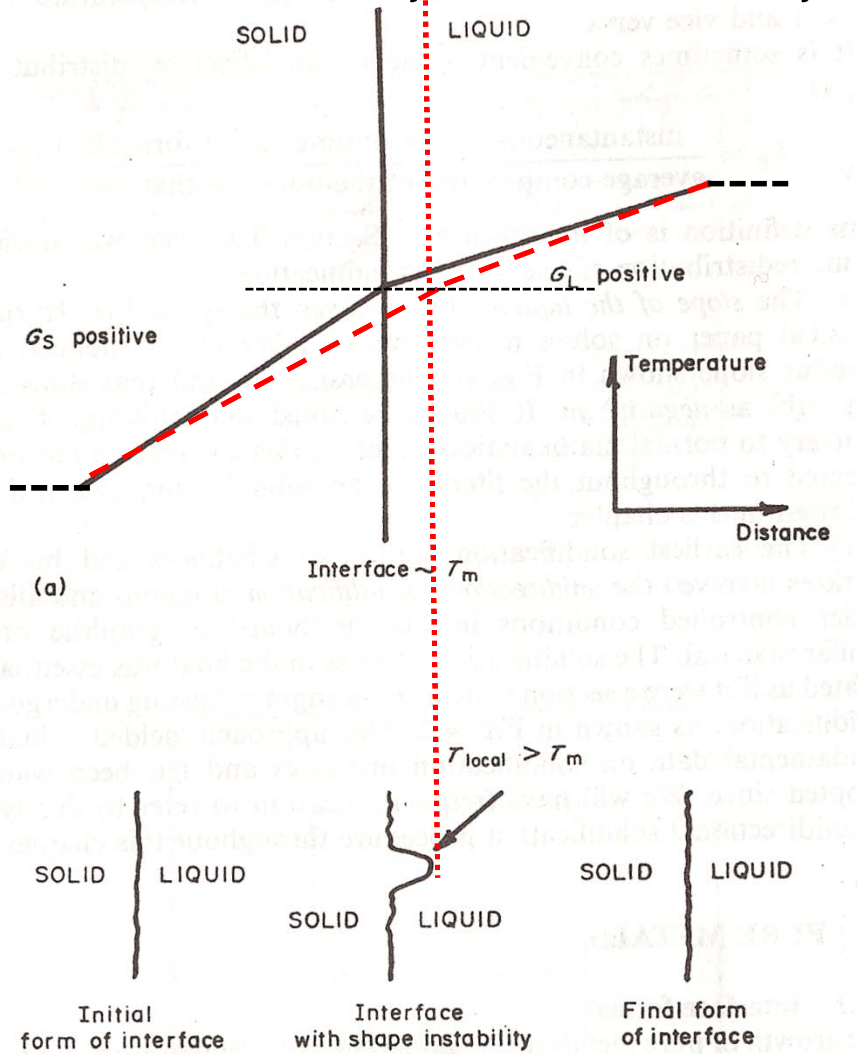
***v* of protrusion ↓ to match other *v* in planar region**

mould walls

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

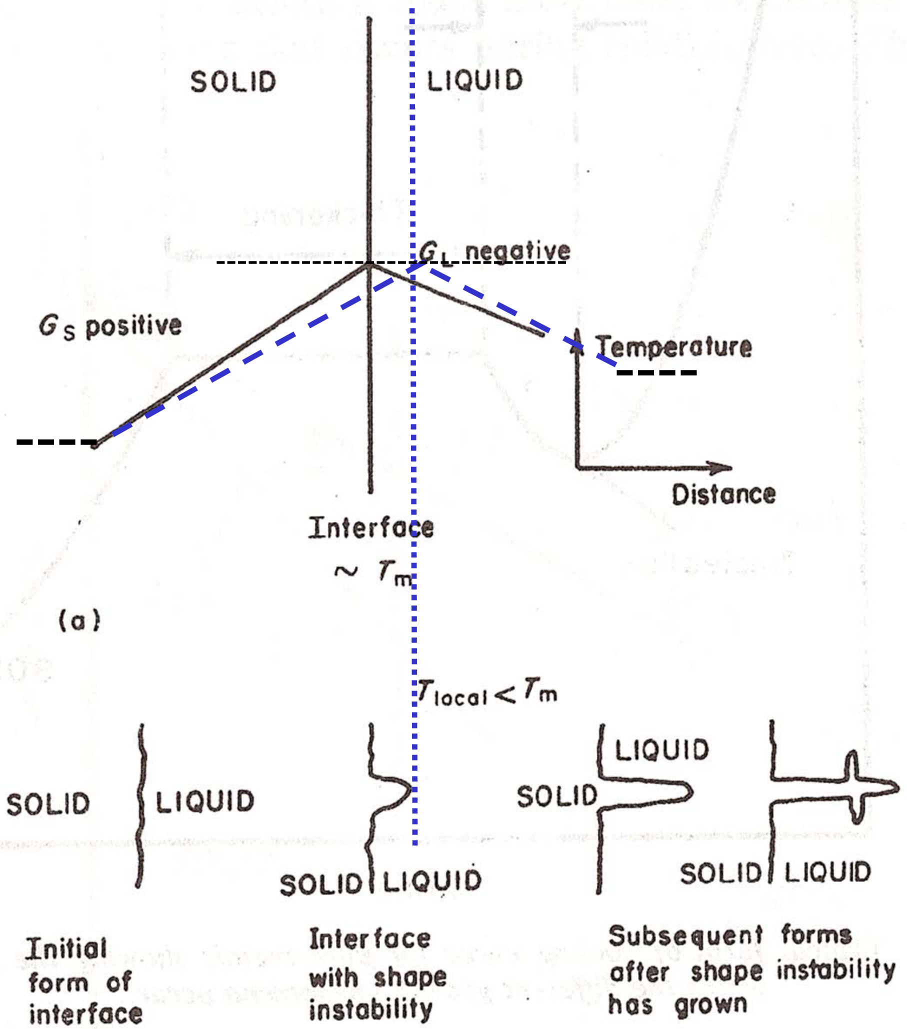
1) Superheated liquid

: Extraction of latent heat by conduction in the crystal



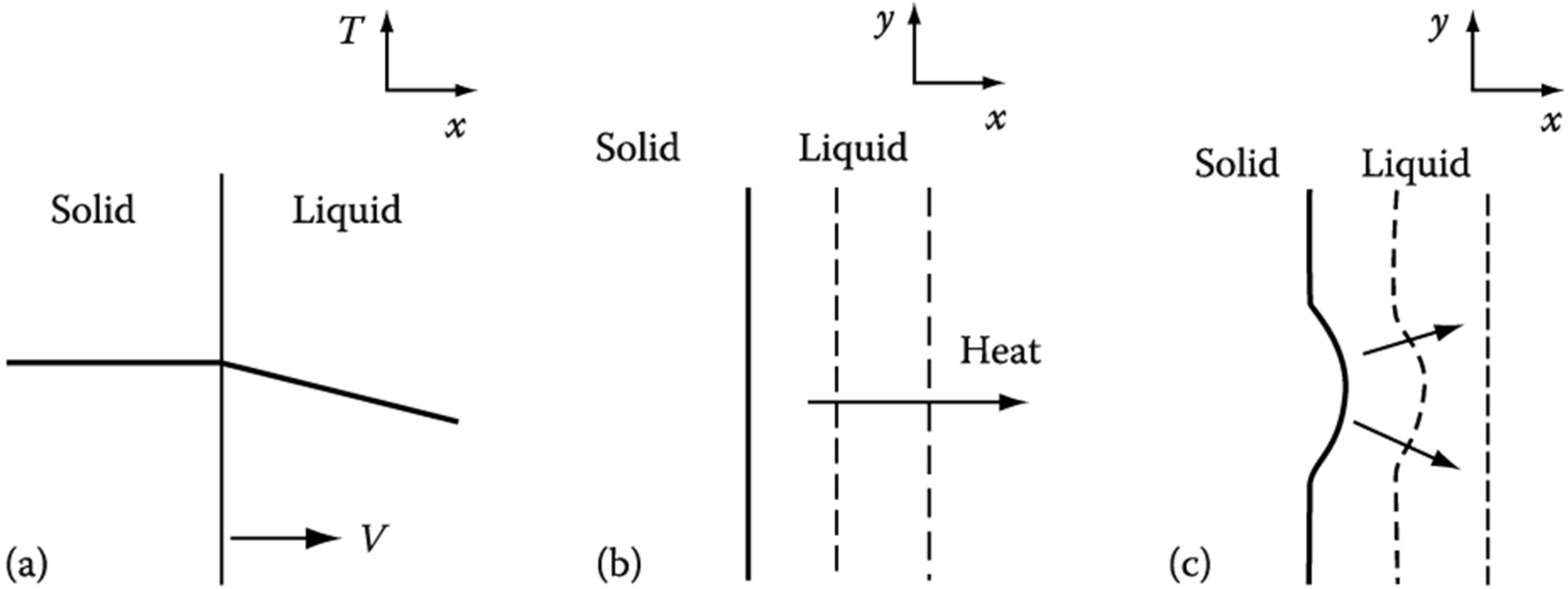
2) Supercooled liquid

: conduction of latent heat into the liquid



Heat Flow and Interface Stability - Planar interface

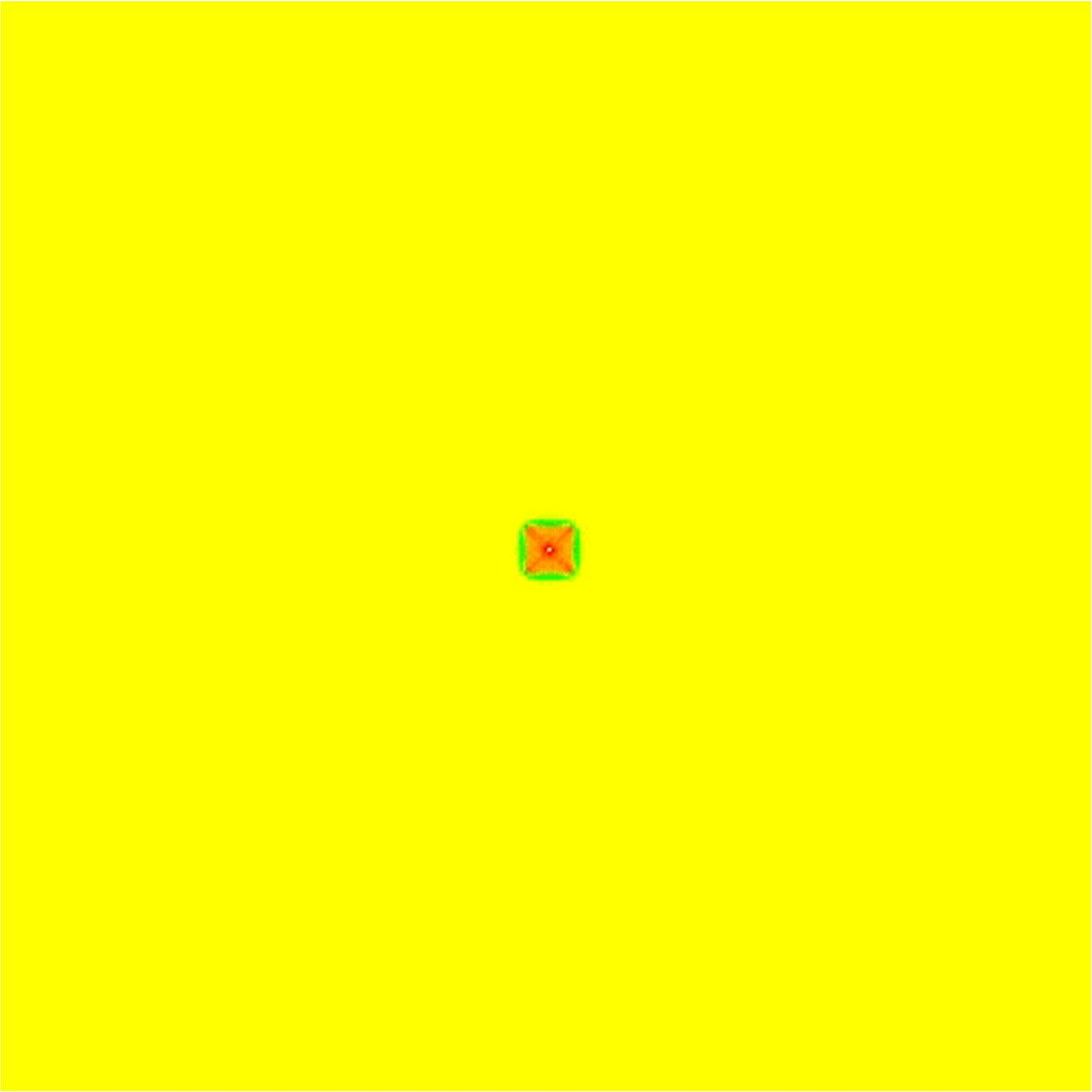
2) Solid growing into supercooled liquid



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

- heat flow from solid = the protrusion grows preferentially.

Solidification: Liquid → Solid



4 Fold Symmetric Dendrite Array

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**

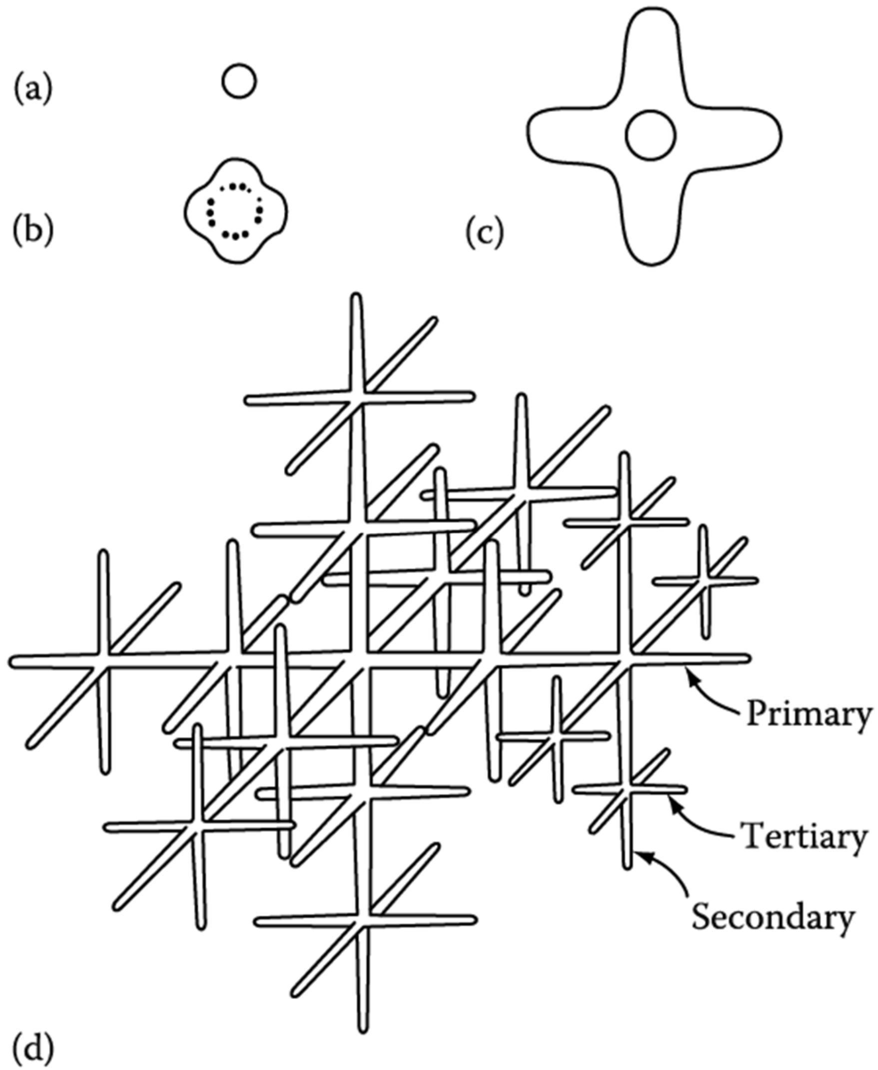


Fig. 4.17 The development of thermal dendrites: (a) a spherical nucleus; (b) the interface becomes unstable; (c) primary arms develop in crystallographic directions (<100> in cubic crystals); (d) secondary and tertiary arms develop

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

Closer look at the tip of a growing dendrite

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

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

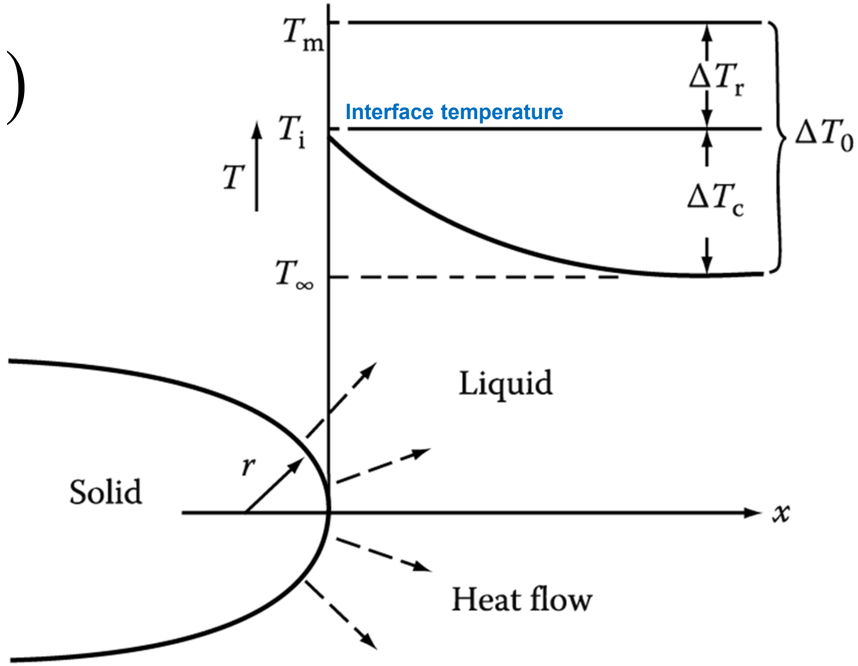
From $K_S T_S' = K_L T_L' + v L_V$

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

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

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

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



However, ΔT also depends on r. How?

Thermodynamics at the tip?

Gibbs-Thomson effect: melting point depression

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

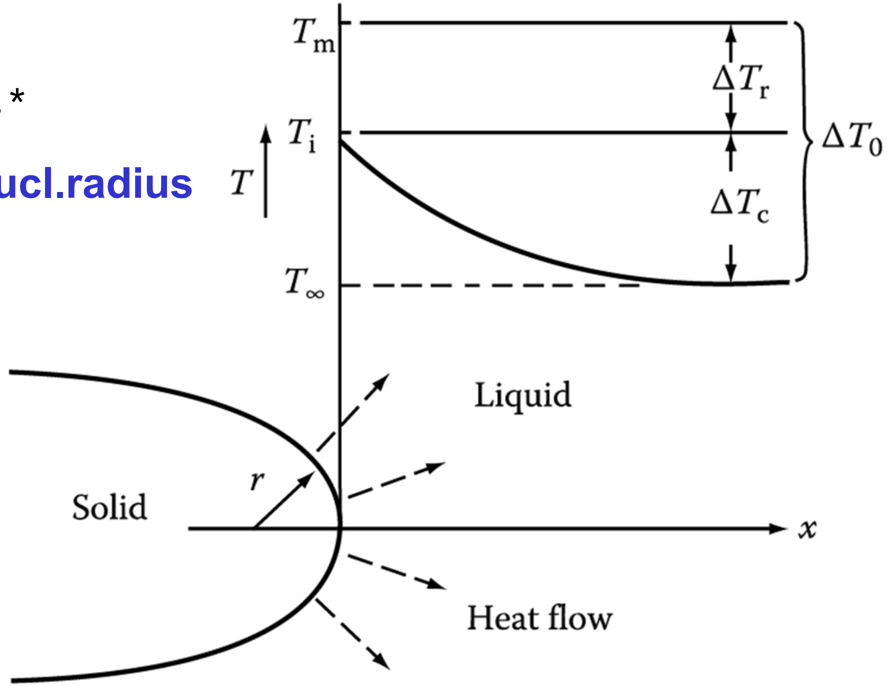
Minimum possible radius (r)?

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

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.

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

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

$v \to 0$ *as* $r \to r^*$ *due to Gibbs-Thomson effect*

as $r \to \infty$ *due to slower heat condution*

Maximum velocity? $\boxed{\to\ r = 2r^*}$